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SOIL SCIENCE

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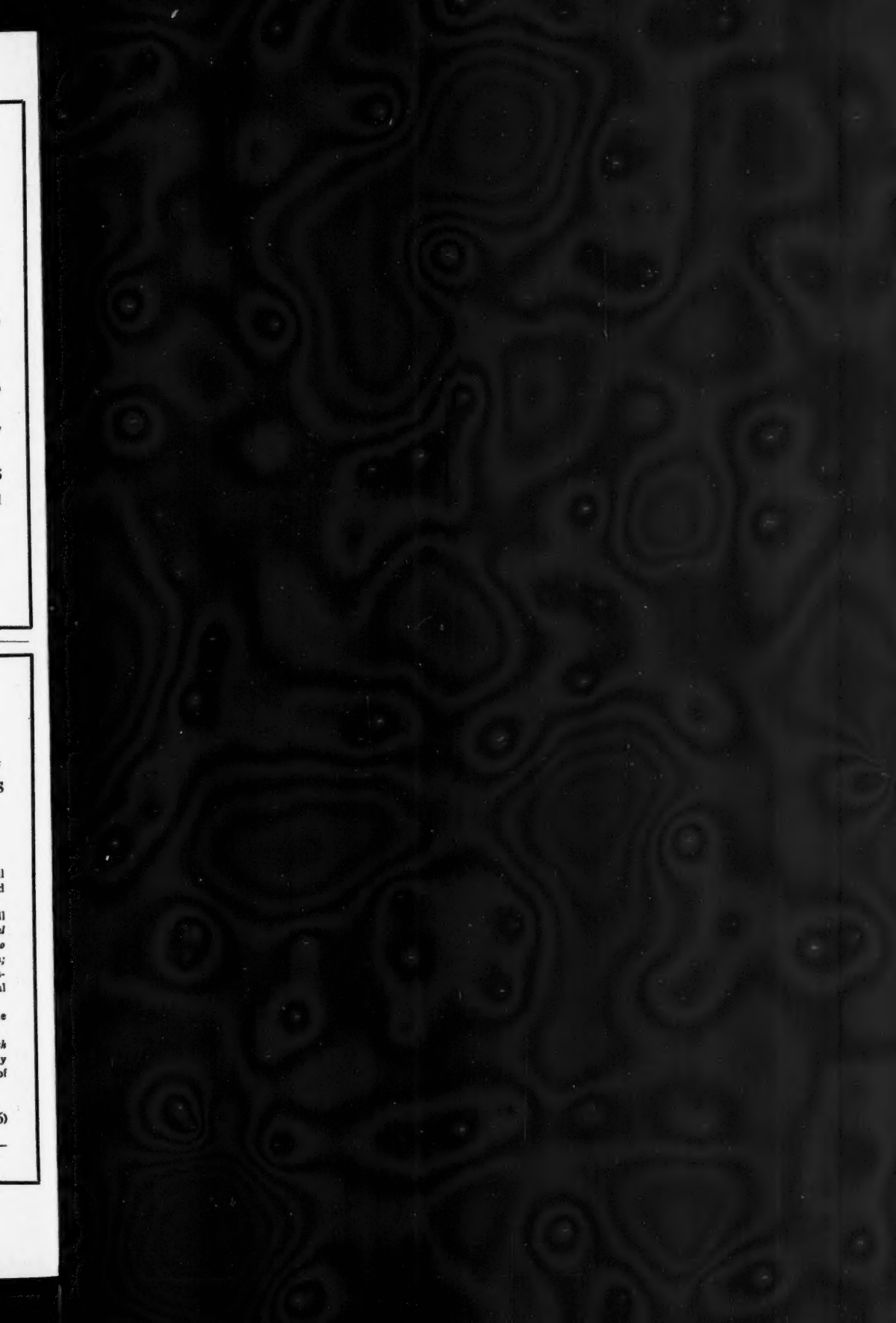

AQUEOUS VAPOR PRESSURE OF SOILS: II. STUDIES IN DRY SOILS

MOYER D. THOMAS

Utah Agricultural Experiment Station

Received for publication August 22, 1923

HISTORICAL

An earlier paper (18) described the vapor pressure as a function of the moisture content, with special reference to comparatively moist soils. The present study is concerned with this function in drier soils, as it is influenced by their chemical composition, size distribution, and previous treatment.

The vapor-pressure moisture relations of soils have been studied to some extent by several investigators, all of whom used the method of allowing small samples to stand in desiccators containing sulfuric acid of known strength and vapor pressure until equilibrium was established after which the moisture content of the soil was determined. If vapor pressure is plotted as ordinate and moisture content as abscissa there is fairly good agreement in the shape of all the published curves. The coarser the texture of the soil the nearer the curves lie to the axis of ordinates. Their upper portions are concave downward, indicating the hyperbolic form already described (18, p. 421). At intermediate pressures they are nearly straight lines, the slope decreasing as the texture becomes finer, while at very low pressures they sometimes show a sharp inflexion as they approach the origin and are concave upward (8). The curves appear to be free from discontinuity such as might be caused by chemical hydrates. Van Bemmelen (19) found this to be true also of the vapor-pressure curves of colloidal silica, alumina, and ferric oxide.

It has been supposed that at a given vapor pressure the moisture is held on the surface of the soil grains by a definite force of attraction which corresponds to definite thickness of water film. It is only necessary, therefore, to determine the moisture content of a soil in equilibrium with an atmosphere of a certain arbitrarily chosen relative humidity in order to arrive at a value which, if it is not directly proportional to the total soil surface, is at least a very useful index of texture. The "hygroscopic coefficient" of Hilgard (10) and Alway (2) and the "hygroscopicity" of Rodewald and Mitscherlich (17) are based on this idea. The latter go so far as to assume, from a study of the heat of wetting, that the moisture absorbed by standing over 10 per cent sulfuric acid is distributed as a mono-molecular film over the soil surface, which they proceed to estimate from a knowledge of the size of a water molecule. Their results have been discredited by Odén (15) and Ehrenberg (7) as being too large and of doubtful significance for comparative purposes if appreciable amounts of colloidal material are present.

An obvious way to test this hypothesis quantitatively is to determine the total surface of the soil from the mechanical analysis and calculate the thickness of the water film. The data on this point in the literature are conflicting. Briggs (4) estimated the thickness of the water film on powdered quartz in an atmosphere of 99 per cent humidity to be 4.5×10^{-4} mm. Patten and Gallagher (16) found the value 3×10^{-4} mm. for soil separate 0.1–0.05 mm. in diameter in a saturated atmosphere. They also obtained results of the same order of magnitude for a number of soils and quote Parks as having given the value, 1.34×10^{-4} mm.,

for glass wool. Odén (14) found that the amount of water per unit of surface at a given vapor pressure varied over a considerable range in different soils and was only constant when the soils compared were nearly identical. The thickness of the water film in a saturated atmosphere was about 2×10^{-5} to 3×10^{-5} mm., whereas at a very low vapor pressure where the curves were inflected toward the origin the thickness was of the order of 10^{-6} mm.

Langmuir's (13) work would indicate that the range of molecular attraction is less than the distance across an ordinary molecule and that therefore a truly absorbed film is never more than one or two molecules thick. The apparent thickness of the films noted above is due to the porous nature of the absorbing surfaces which hold part of the water by capillarity. Harkins and his coworkers (9) have developed a general thermo-dynamic criterion of film formation called the "coefficient of spreading," based on the surface tensions of the absorbing and absorbed substances and their interfacial tension. According to the numerical value of this "coefficient" a film may not form at all or its thickness may range from mono-molecular dimensions up to a micron, though thick films are probably rare. Unfortunately, the application of this criterion at present is precluded by the lack of surface tension data for solids.

The Bureau of Soils (1) has recently proposed absorption of water over 2 per cent sulfuric acid as a method of estimating the amount of "colloidal" material in soil.

TABLE 1

Description of the natural Utah soils

LABORATORY NUMBER	TYPE NAME	CLASS	SOURCE	DEPTH OF SAMPLE	STRUCTURE	SOLUBLE SALTS
			County			*per cent*
T1	Trenton	Clay	Cache	Subsoil		0.126
G1*	Millville	Silty clay loam	Cache	Surface soil		0.038
WL.†	Millville	Clay loam	Cache	Surface soil		0.130
B5		Sandy loam	Davis	Surface soil		
168‡	Naples	Clay loam	Uinta	0–$\frac{1}{8}$ in.	Crust	0.050
169‡	Naples	Clay loam	Uinta	$\frac{1}{8}$–1 in.	Plate structure	0.060
170‡	Naples	Clay	Uinta	1–6 in.	Pea structure	0.060
172‡	Naples	Clay	Uinta	9–15 in.	Compact layer	0.100
507‡	Abbott	Clay	Millard	0–$\frac{1}{8}$ in.	Crust	0.120
508‡	Abbott	Clay	Millard	$\frac{1}{8}$–4 in.	Compact layer	.....
629‡	Bennett	Sandy loam	Uinta	$\frac{1}{8}$– 2 in.	Mulch	.....
631‡	Bennett	Sandy clay	Uinta	18–24 in.	Compact layer	.....
993‡	Cache	Clay	Cache	0–4 in.		1.520
994‡	Cache	Clay	Cache	4–10 in.		1.580

* From Greenville Farm.

† From West Logan.

‡ Part of virgin profile.

DESCRIPTION OF THE SOILS

Source

The vapor-pressure moisture relations reported below were investigated in three stages:

(1) A group of chemically similar soil separates ranging from fine sands to tight clays was first studied. These soils form a part of a series prepared by W. Gardner of this station from Trenton clay by elutriation. They are numbered S5–S19 to indicate their order of preparation, the larger numbers representing finer textures. In preparing them it was

TABLE 2

Chemical analysis of the soils (dried at 110°C.)

	SOIL S7	SOIL SW7	SOIL S13	SOIL S15	SOIL S18	SOIL TRENTON	SOIL T7	SOIL G1	SOIL W.L.	SOIL 168	SOIL 169	SOIL 170	SOIL 172	SOIL 508	SOIL 629	SOIL 631	SOIL 994	SOIL B5
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
SiO_2	44.28	43.40	43.94	43.50	42.23	40.10	51.25	39.40	49.70	67.62	65.21	60.26	61.26	49.12	90.02	81.05	50.50	64.90
CO_2	21.20	22.72	16.38	15.50	15.30	15.63	2.36	18.30	14.40	4.68	4.90	5.58	6.26	8.66	0.14	0.45	8.85	0.00
Al_2O_3	4.42	2.40	8.57	9.75	10.72	9.79	18.52	7.65	7.14	8.98	9.60	11.19	9.73	12.24	2.99	7.71	11.31	11.51
Fe_2O_3	1.31	1.50	3.20	3.86	3.90	3.88	6.56	3.26	2.65	2.70	3.43	3.60	3.31	5.30	1.72	3.27	3.65	6.47
CaO	16.18	17.10	15.41	14.90	15.71	17.80	3.71	13.46	12.60	5.90	6.33	7.81	7.98	10.34	0.45	1.21	11.35	2.83
MgO	9.24	9.80	6.70	6.13	5.46	5.05	5.48	9.90	6.55	2.55	2.80	3.14	3.26	4.92	0.86	1.35	3.82	2.34
Na_2O	0.47	0.56	0.56	0.42	0.42	0.52	0.20	0.51	0.66	0.80	0.84	0.82	0.83	0.26	0.66	0.68	1.62	1.63
K_2O	1.36	1.50	1.89	1.97	2.29	2.50	3.77	2.25	1.76	2.30	2.60	2.72	2.45	2.64	1.06	1.48	2.31	2.29
H_2O	0.81	0.53	2.37	2.88	3.33	3.52	6.90	3.22	2.46	2.82	3.30	4.26	3.30	5.50	1.25	2.32	4.38	4.21
TiO_2	0.34	0.37	0.48	0.50	0.51	0.47	0.62	0.46	0.46	0.69	0.61	0.58	0.74	0.62	0.34	0.53	0.63	1.01
P_2O_5	0.17	0.17	0.19	0.20	0.23	0.20	0.20	0.25	0.29	0.18	0.26	0.23	0.225	0.24	0.25	0.09	0.36	0.26
SO_3	0.04	*	0.05	0.052	0.088	0.05	*	0.031	0.05	0.002	0.004	0.004	0.012	*	*	*	0.03	*
Cl	*	*	*	*	*	0.02	*	0.008	Trace	0.00	0.00	0.00	0.00	*	*	*	1.08	*
CrO_3	*	*	*	*	*	0.005	*	0.005	0.005	*	*	*	*	*	*	*	*	*
MnO	0.025	†	0.041	0.052	0.06	0.06	†	0.07	0.056	†	†	†	†	†	†	†	†	†
SrO	*	*	*	*	*	Trace	*	Trace	Trace	*	*	*	*	*	*	*	*	*
BaO	*	*	*	*	*	0.04	*	0.036	0.036	*	*	*	*	*	*	*	*	*
N	*	*	0.036	0.036	0.05	0.075	*	0.14	0.10	0.07	0.044	0.035	0.033	0.079	0.035	0.055	0.05	0.10
C	0.25	0.11	0.44	0.40	0.20	0.68	0.33	1.62	1.32	0.41	0.22	0.29	0.36	0.75	0.33	0.53	0.49	2.55
Total	100.10	100.16	100.26	100.15	100.50	100.39	99.90	100.57	100.24	99.70	100.15	100.52	99.75	100.67	100.10	100.72	100.47	100.10

* Not determined.

† Present, but not determined quantitatively.

hoped to obtain material having only a small range of size of particles, but the failure to use deflocculating agents in the elutriator defeated this hope. Nevertheless, they offer a good opportunity to study the influence of texture on vapor pressure when the chemical composition is approximately constant.

(2) The Trenton clay was next considered after subjecting it to a number of wetting and drying treatments.

(3) Finally the inquiry was carried to a group of nineteen other natural and artificial soils representing a wide range of texture, mechanical distribution, and chemical composition. The natural soils were supplied by D. S. Jennings of this station. They are described in table 1. The artificial soils were true separates numbered S.W.5–S.W.9 and were made from the corresponding soils of Gardner's series by shaking them for several hours with 1 per cent sodium carbonate and subsequently decanting. This process was repeated many times to remove the colloidal content. Soils T5, T6, and T7 were prepared from Trenton clay by sedimentation. Soil T5 was free from removable colloid and had sharp limits of size between 0.5 and 1.5 micron radius. When dried it formed a soft cake which could be easily disintegrated to a fluffy white powder. Soils T6 and T7 were highly colloidal. When dried they formed hard, polished horn-like cakes. Soil T6 was brownish gray in color, while T7 was dark brown.

Chemical composition

Complete chemical analyses of all the soil types are given in table 2. The soils range from highly calcareous to highly silicious materials. They are generally low in organic matter although three contain moderate amounts. Gardner's separates show an increase in the iron, alumina, potassium, and water and a decrease in the silica, magnesium, and carbonate carbon as the texture becomes finer, but the differences are slight. These changes are very marked in soil T7, but the low value of the carbonate is probably due in part to the fact that in its preparation the colloidal suspension was coagulated by carbon dioxide which dissolved part of the lime. The range of the carbonate content in the other soils is noteworthy. It should be pointed out that the two Cache soils differ noticeably in the respect and that soil 993 contained only 0.96 per cent carbon dioxide.

Mechanical composition

Complete mechanical analyses of all the soils have been made by the method recently developed at this station (11). The data are given graphically in figure 1 in which the ordinate shows the percentage of material of smaller radius than the value of the corresponding abscissa. The curves appear to extrapolate to the zero ordinate at about 0.01 micron radius, and this extrapolation has been made use of in calculating the total surfaces of the soils. Gardner's separates are shown in chart A. They fall in the expected order. Soil 631 is particularly interesting because it is almost entirely lacking in silt.

In carrying out the analyses every effort was made to secure complete dispersion. Two hours of shaking with 0.5 per cent sodium carbonate was not sufficient to deflocculate a sample of heavy soil which had been oven-dried or thoroughly air-dried. This is indicated in the insert in chart C, figure 1, which shows the result of these treatments on Trenton clay. It seems evident, therefore, that drying a soil makes its texture coarser, in effect, by dehydrating the colloids and making them adhere more firmly to the larger particles. Prolonged shaking or contact with water will reverse this condition. In the analyses reported in this paper the samples were allowed to stand moist for several weeks, after which they were shaken for eight to fifteen hours with 0.5 per cent sodium carbonate. If the soil contained an appreciable amount of soluble salt this was removed by decantation before shaking.

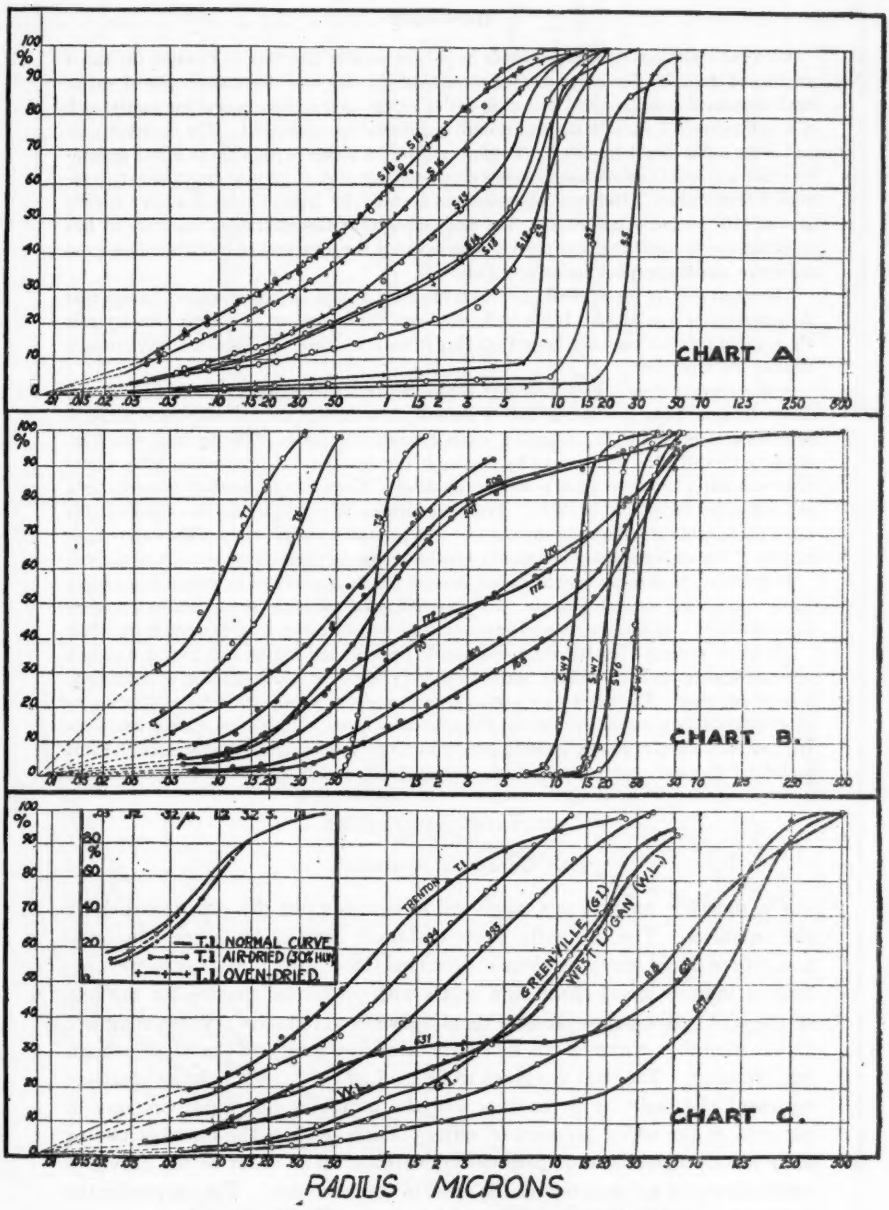

FIG. 1. MECHANICAL COMPOSITION OF THE SOILS

The ordinate represents the percentage of material of smaller radius than the value of the corresponding abscissa. The insert in Chart C illustrates the effect of drying treatment on the mechanical analysis.

TECHNIQUE

Both the static and dynamic methods have been used in this work to measure the vapor pressure of the soil. The static method consists in exposing 5-to 10-gram samples of soil in small aluminum cans, provided with close-fitting covers, over sulfuric acid of known strength in a well exhausted vacuum desiccator until equilibrium is established. The moisture content of the soil is then determined. Twenty to thirty cans may be placed in an 8-inch desiccator which is stored in an insulated box in a deep basement room to prevent appreciable fluctuations of temperature. Moisture determinations are made by drying the soil in a large electric oven at 110° for forty-eight hours. The most important considerations for accuracy in this operation are to cover the cans quickly after opening the oven and to cool them in a good desiccator containing phosphorus pentoxide.

The apparatus for the dynamic method is the same as that already described, except that the presaturator is enlarged. It has been found expedient, however, in dealing with dry soils whose vapor pressure are much lower than that of water to adopt the Washburn (20) arrangement of the experiment:

A slow current of air is passed through the presaturator containing a sulfuric acid solution about the same vapor pressure as that of the soil, then through the soil sample contained in large brass tubes, and finally through a weighed moisture absorber. The dry air is now completely saturated with water vapor by passing it through a series of horizontal tubes partly filled with water and dried again in another absorber. The whole apparatus is immersed in a well controlled thermostat at 25°C. From the increase in weight of the two absorbers the vapor pressure of the soil may be calculated. The preliminary adjustment of the water-vapor content of the air is necessary in order to avoid a change in the moisture content of the soil.

In practice, the same air may be passed through two or more sets of soil tubes before being finally saturated in the water vessel. The pressure in each section of the apparatus is read on oil manometers. In this way several vapor-pressure measurements may be made at one time.

The static method is less laborious, operates on a smaller soil sample, and, provided enough cans and desiccators are available, permits the carrying out of a large number of determinations at one time. Though it may require several weeks or even months for equilibrium to be established in a given experiment, the apparatus needs no attention during this time. The two methods give closely agreeing results with dry and moderately moist soils, but it is doubtful if the static process is sufficiently accurate or rapid to be used in studying moist soils.

EXPERIMENTAL RESULTS

Gardner's separates

The dynamic method was employed in carrying out the experiments with the separates. The dry soils were uniformly wetted by successive small amounts of liquid water, as already described (18, p. 415). After each wetting, the soil samples stood closed in a bottle with occasional shaking for three to seven days before vapor-pressure measurements were made. When complete curves were thus obtained the soils were dried in the air and the whole process was repeated. The data are given in figure 2, chart A, in which the abscissae represent the moisture percentage and the ordinates the vapor pressure in per cent of the vapor pressure of water. Each point is the mean of two or more closely agreeing duplicate determinations. The order of the curves is qualitatively in agreement with the order of the separates. The curves for the soils S13 to S19, inclusive, are shifted very materially to the right as a result of wetting and subsequently air-drying. This is due to the fact that these

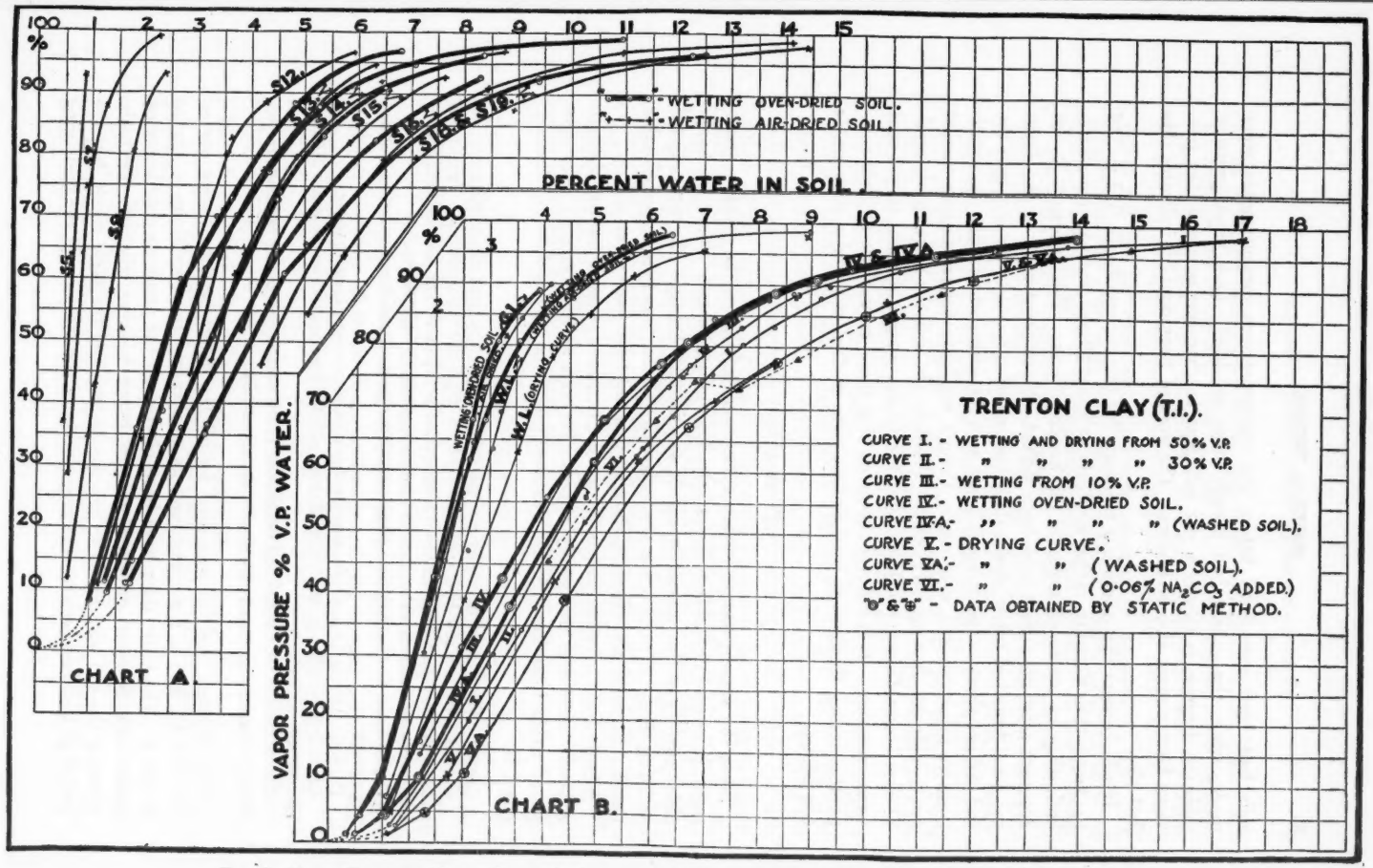
WETTING OVEN-DRIED SOIL.
WETTING AIR-DRIED SOIL.
PERCENT WATER IN SOIL.
VAPOR PRESSURE % V.P. WATER.
CHART A.
CHART B.
TRENTON CLAY (T.I.).
CURVE I. - WETTING AND DRYING FROM 50% V.P.
CURVE II. - " " " " 30% V.P.
CURVE III. - WETTING FROM 10% V.P.
CURVE IV. - WETTING OVEN-DRIED SOIL.
CURVE IV-A. - " " " " (WASHED SOIL).
CURVE V. - DRYING CURVE.
CURVE V-A. - " " (WASHED SOIL).
CURVE VI. - " " (0.06% Na_2CO_3 ADDED)
"o" & "o" - DATA OBTAINED BY STATIC METHOD.

FIG. 2. VAPOR PRESSURE DATA: CHART A, GARDNER'S SEPARATES; CHART B, TRENTON CLAY AND MILLVILLE SOILS

The curves illustrate the influence of the previous history of a soil on its vapor pressure and moisture relations

soils had been oven-dried before the vapor-pressure measurements were made, while the others had merely been air-dried. One vapor-pressure moisture diagram is therefore not sufficient to characterize a soil: the previous history must also be known. The work of Beaumont (3) indicates this fact also.

It will be seen that there is a tendency for the curves of soils S13 to S19 to change their direction rather suddenly at about 60 per cent vapor pressure, indicating an increased capacity for holding water. This tendency is not apparent after the curves have been shifted. Subsequent work on the Trenton clay, described below, shows that this condition is due to the fact that the soil had not always come to equilibrium with the added water when the vapor-pressure measurements were made, though duplicate determinations carried out on different days agreed closely. The drier the soil, the more slowly equilibrium is established, which accounts for the sharp angle at about 60 per cent vapor pressure. It is believed, however, that these curves are entirely comparable among themselves because they were worked out under comparable conditions.

Trenton clay

Since the vapor-pressure moisture function depends on the previous treatment, it seemed desirable to investigate it in greater detail. Since the available quantity of the heavier separates was limited, Trenton clay was selected as being likely to exhibit the characteristics of this function in considerable detail. Physical and chemical data on this soil have been given above.

A large, fresh, air-dried (about 50 per cent humidity) sample was put through a ½-mm. sieve and thoroughly mixed. Portions of this material were subjected to the following different treatments with the results shown in figure 2, chart B:

Curve 1. Wetting and drying by successive stages from 50 per cent vapor pressure.

Curve 2. Wetting and drying progressively from 30 per cent vapor pressure. Part of this material had previously been moistened to saturation by capillarity and part had been shaken with 2 per cent ammonia water, the two treatments giving identical results.

Curves 3 and 4. Wetting from 10 per cent vapor pressure and the oven-dried condition, respectively.

Curve 5. Drying by successive amounts from complete saturation with water.

Curve 6 Drying progressively after shaking with 0.025 per cent sodium carbonate (0.06 per cent on basis of dry soil).

Curves 4A and 5A. Subjecting washed soil to the wetting and drying processes, respectively, in the static process as described in the next section.

The dynamic method was used for all the determinations except curves 4A and 5A and a few measurements duplicating the conditions in curves 4 and 5. The latter data have been plotted on the graph as double-circled points and indicate satisfactory concordance between the two methods. Wetting the soil with liquid or gaseous water gives the same result, but the period of standing between the preparation of the sample and the measuring

of its vapor pressure seems to be important. In curve 1 this period was six months, but in the other work it was one to two months. For example, in curve 2 the period was six weeks. Two months later, three of the points on this curve were redetermined, as indicated by the small arrows. The driest soil (50 per cent vapor pressure) showed an appreciable shift, but equilibrium had apparently been reached with the others. This explains the shape of some of the curves obtained for the soil separates as noted above.

The data prove conclusively that the vapor-pressure moisture function depends on the previous history of the soil. Drying is particularly effective in raising the vapor pressure, that is, in making the texture appear coarser. The extent of this action depends on the extent of the drying. The mechanical analysis shows this action in a measure as well. It is thus possible for a sample of Trenton clay to stand in equilibrium with another sample of the same soil containing one-fourth to one-third more water.

Curves 1–4 are strikingly similar in shape, maintaining a constant distance between themselves and converging at high and very low vapor pressures. On the other hand, curves 5 and 6 seem to show that while the texture of the soil at high moisture contents may appear finer than that indicated by curve 1, below 70 per cent vapor pressure this curve represents the maximum dispersion for this soil in its natural state. The abnormal shape of curve 6 is probably to be explained by the flocculating action of the sodium carbonate when it became sufficiently concentrated by the evaporation of the water. This explanation will also apply to the difference between curves 4 and 4A and curves 5 and 5A. The method, therefore, gives promise of furnishing a quantitative means of studying the action of salts on the structure of soil and is being investigated further from this point of view.

The diverse group of soils

The other soils were all studied by the static method. Four series of observations were made. One set of samples was oven-dried and allowed to take up water in the desiccators (wetting curves). Another set was moistened by capillarity for two weeks and then allowed to dry out in the desiccators (drying curves). A larger sample of each soil was treated with water containing carbon dioxide and washed by decantation with distilled water until the colloid commenced to deflocculate. The material was then divided and both its wetting and drying curves determined. Except in the case of soils 993 and 994, which contained a large amount of soluble salt and soil T1, which has already been discussed, washing was without influence on the curves.

The results are given graphically in figure 3. The following anomalies are noticeable:

1. The drying curve of B5 is proportionately farther away from its wetting curve than is the case with the other soils.
2. The wetting curves of soils 170 and 172 converge at high vapor pressure and the drying curves actually cross

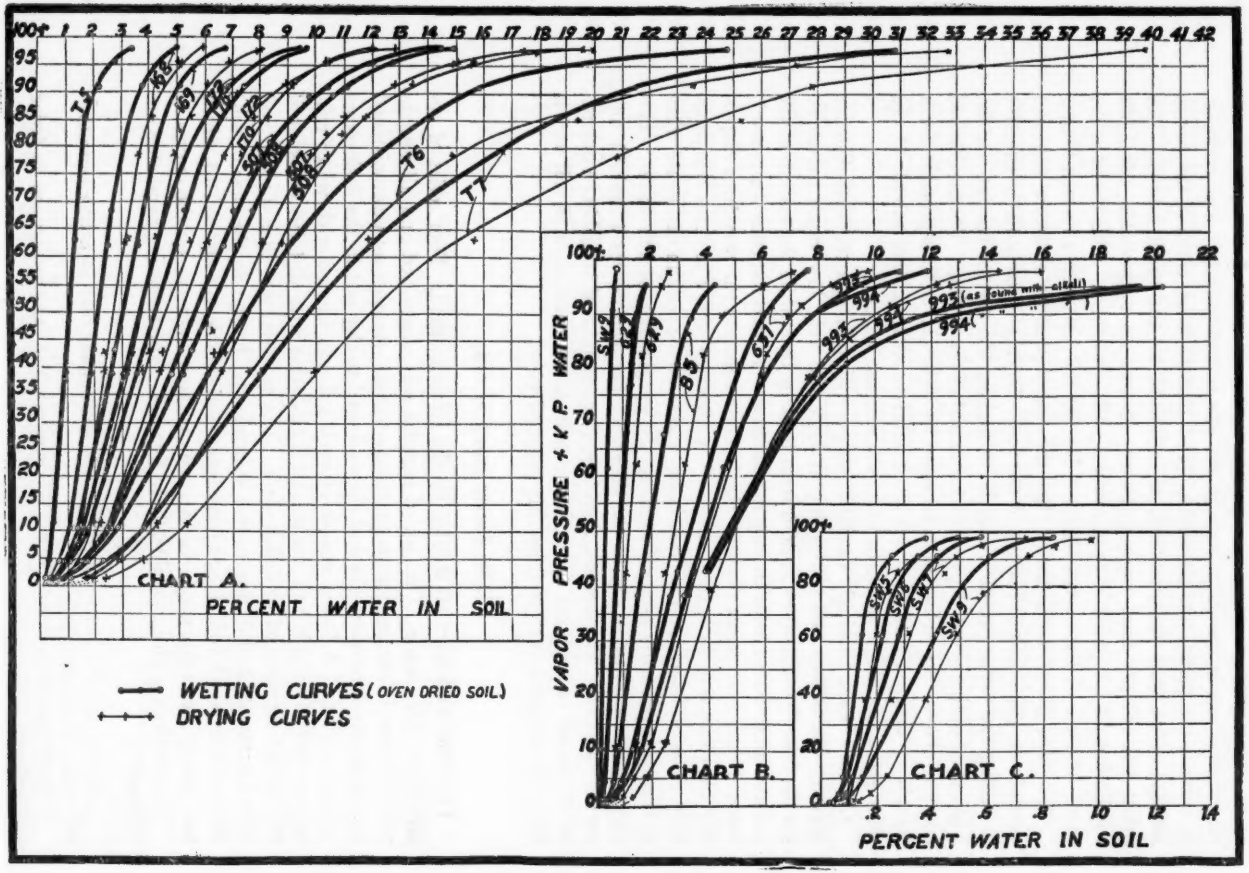

FIG. 3. VAPOR PRESSURE DATA FOR THE DIVERSE GROUP OF SOILS

The effect of wetting from the oven-dry condition and drying from complete saturation with water is shown in each case

3. Soils 993 and 994 are almost coincident over most of their course, but they diverge appreciably on their upper portions. The wetting curves of these soils, as they were found impregnated with soluble salt (mainly sodium chloride) are also shown. The position of these curves indicates that all the salt is dissolved in the soil solution when more than 10 per cent moisture is present.

4. Even the coarse, well washed, separates show the inflection toward the origin at low vapor pressure (chart C, fig. 3).

DISCUSSION

Comparison of the vapor-pressure curves

It is evident from figure 3 that the drying curves are steeper than the wetting curves. Moreover, soils 508 and T7 belong to different families. In order to bring out the relationships existing between the curves, the moisture content of each soil has been divided by the corresponding value for either washed Trenton clay, or soil 508, on a number of different isobars. The results are given in tables 3 and 4. The ratios are approximately constant from 10 to 95 per cent vapor pressure for each soil treatment, and though different treatments change both the slope and position of the curves, the ratios are unaffected by these changes, that is, the curves are all shifted proportionately. Soil B5 is an exception, due perhaps to its higher organic matter content. The whole group of soils may therefore be divided into two families. A few individuals take a somewhat intermediate position, usually favoring one system more than the other.

It is difficult to assign a reason for the two families of curves. It may be noted, that the Trenton series is comprised for the most part of derivatives of Trenton clay together with the closely related Cache soils. On the other hand, the closely related Millville soils and the washed separates fall in the Abbott series. A chemical correlation seems hopeless. The carbonate content is apparently without significance because of its wide range in both families. A more probable explanation is to be found in the relative amounts of colloidal and silty material in the soils. In the last column of table 5, the surface of the particles larger than 0.1 micron has been divided by the total surface. In the Trenton series the quotient lies between 0.1 and 0.25, while in the Abbott it ranges from 0.25 to 1.0. The soils which give intermediate ratios, notably soils W. L. and S15, also occupy an intermediate position between the two families of curves. The only disturbing exception to this rule is soil T5 which is entirely very fine silt or coarse clay. It would seem therefore that when the colloidal surface is greatly in excess of the silty surface, the absorption at low pressures is repressed.

Vapor pressure and total surface

There is considerable evidence, as already pointed out, to indicate that the moisture contents of a series of soils on a given isobar are not necessarily proportional to their total surfaces. The present investigation offers a good opportunity for studying this question.

The effect of wetting from the oven-dry condition and drying from complete saturation with water is shown in each case

TABLE 3

Comparison of vapor-pressure curves—$\frac{H_2O \text{ in soil}}{H_2O \text{ in soil T1}}$ on isobars

WETTING CURVES, AIR-DRIED SOIL NO. T1 = 1.00

VAPOR PRESSURE	H_2O IN T1	SOIL W.L.	SOIL G1	SOIL S5	SOIL S7	SOIL S9	SOIL S12	SOIL S13	SOIL S14	SOIL S15	SOIL S16	SOIL S18
per cent	*per cent*											
95	10.68	0.477	.....	.....	0.136	.....	0.440	0.515	0.608	.....	0.805	0.935
90	9.68	0.506	0.427	0.084	0.137	0.222	0.457	0.562	0.630	0.712	0.836	0.955
85	8.50	0.491	0.426	0.091	0.136	0.223	0.443	0.571	0.625	0.718	0.833	0.937
80	7.60	0.487	0.429	0.097	0.132	0.228	0.456	0.575	0.633	0.724	0.850	0.924
70	6.46	0.496	0.437	0.103	0.132	0.236	0.480	0.570	0.648	0.721	0.859	0.950
60	5.50	0.534	0.468	0.109	0.140	0.247	0.498	0.594	0.665	0.751	0.885	0.975
55	5.10	0.540	0.472	0.112	0.143	0.251	0.503	0.600	0.674	0.760	0.892	0.985
Mean	55–95	0.504	0.443	0.099	0.137	0.235	0.468	0.570	0.640	0.731	0.851	0.951

WETTING CURVES, OVEN-DRIED SOIL NO. T1 = 1.00

VAPOR PRESSURE	H_2O in T1	SOIL W.L.	SOIL G1	SOIL 508	SOIL 993	SOIL 994	SOIL T5	SOIL T6	SOIL T7	SOIL S13	SOIL S14	SOIL S15	SOIL S16	SOIL S18
per cent	*per cent*													
95	11.05	0.500	.....	1.14	0.852	0.905	0.256	1.71	2.24	0.540	0.644	0.683	0.842	0.952
90	8.70	0.517	0.460	1.24	0.909	0.920	0.253	1.78	2.38	0.571	0.642	0.723	0.864	0.978
85	7.50	0.525	0.460	1.30	0.940	0.940	0.260	1.85	2.46	0.602	0.654	0.741	0.885	0.980
80	6.80	0.513	0.452	1.33	0.941	0.941	0.258	1.83	2.47	0.607	0.670	0.738	0.874	0.960
70	5.68	0.532	0.475	1.39	0.931	0.931	0.256	1.82	2.43	0.594	0.651	0.756	0.870	0.950
60	4.80	0.532	0.508	1.45	0.935	0.935	0.265	1.81	2.42	0.587	0.643	0.783	0.878	0.980
50	4.15	0.541	0.517	1.45	0.937	0.937	0.268	1.77	2.35	0.582	0.663	0.782	0.865	0.956
35	3.16	0.563	0.550	1.52	0.965	0.965	0.272	1.80	2.34	0.580	0.686	0.781	0.870	0.975
20	2.28	0.567	0.547	1.53	0.962	0.962	0.272	1.78	2.33	0.601	0.704	0.780	0.885	0.977
10	1.68	0.578	0.547	1.49	0.950	0.950	0.268	1.64	2.18	0.630	0.732	0.802	0.893	1.000
Mean	10–95	0.537	0.502	1.38	0.933	0.938	0.264	1.78	2.36	0.589	0.667	0.757	0.873	0.970

DRYING CURVES NO. T1 = 1.00

VAPOR PRESSURE	H_2O IN T1	SOIL W.L.	SOIL G1	SOIL 508	SOIL 993	SOIL 994	SOIL T5	SOIL T6	SOIL T7
per cent	*per cent*								
98	19.4	0.470	....	1.05	0.747	0.825	....	1.69	2.05
95	14.5	0.461	....	1.07	0.835	0.856	....	1.85	2.28
90	11.25	0.471	....	1.15	0.897	0.920	....	1.93	2.36
85	9.87	0.481	....	1.18	0.901	0.922	....	1.82	2.38
80	8.80	0.490	....	1.21	0.892	0.915	....	1.76	2.44
70	6.97	0.537	....	1.36	0.947	0.969	.....	1.83	2.50
60	5.95	0.565	....	1.43	0.958	0.975	....	1.83	2.40
50	5.13	0.577	....	1.48	0.955	0.975	....	1.79	2.34
35	4.14	0.572	....	1.49	0.960	0.975	....	1.70	2.22
20	3.15	0.570	....	1.52	0.960	0.980	....	1.68	2.17
10	2.43	0.571	....	1.54	0.965	0.985	....	1.65	2.06
5	1.85	0.615	....	1.54	0.965	1.000	....	1.62	2.02
Mean	10–95	0.530	....	1.34	0.920	0.947	....	1.78	2.32

TABLE 4

Comparison of vapor-pressure curves $\frac{H_2O \text{ in soil}}{H_2O \text{ in soil } 508}$ *on isobars*

WETTING CURVES—OVEN-DRIED SOIL (508 = 1.00)

VAPOR PRESSURE	H_2O in 508	SOIL SW5	SOIL SW6	SOIL SW7	SOIL SW9	SOIL G1	SOIL W.L.	SOIL B5	SOIL 168	SOIL 169	SOIL 170	SOIL 172	SOIL 629	SOIL 631	SOIL 507
per cent	*per cent*														
98	14.95	0.0255	0.0335	0.0390	0.0560	.....	0.426	.....	0.340	0.452	0.650	0.630	.....	0.522	0.970
95	12.55	0.0255	0.0335	0.0390	0.0550	.....	0.430	0.332	0.350	0.464	0.680	0.630	0.141	0.550	0.950
90	10.82	0.0227	0.0315	0.0384	0.0545	0.369	0.417	0.321	0.340	0.470	0.670	0.615	0.140	0.558	0.932
85	9.78	0.0213	0.0316	0.0378	0.0550	0.354	0.402	0.320	0.343	0.474	0.666	0.604	0.143	0.562	0.928
80	9.02	0.0205	0.0305	0.0388	0.0560	0.342	0.382	0.320	0.344	0.480	0.677	0.597	0.142	0.567	0.920
70	7.90	0.0203	0.0306	0.0397	0.0575	0.342	0.376	0.317	0.343	0.500	0.690	0.597	0.142	0.560	0.930
60	6.95	0.0207	0.0312	0.0403	0.0580	0.350	0.369	0.317	0.352	0.503	0.690	0.603	0.138	0.552	0.932
50	6.02	0.0219	0.0320	0.0412	0.0588	0.358	0.374	0.316	0.360	0.506	0.697	0.602	0.135	0.540	0.945
35	4.80	0.0239	0.0323	0.0417	0.0582	0.362	0.371	0.292	0.374	0.502	0.682	0.594	0.131	0.525	0.940
20	3.48	0.0278	0.0345	0.0430	0.0582	0.370	0.384	0.302	0.379	0.505	0.680	0.588	0.131	0.518	0.940
10	2.51	0.0334	0.0386	0.0470	0.0595	0.340	0.356	0.299	0.397	0.516	0.685	0.595	0.132	0.518	0.947
5	1.64					0.384	0.384	0.366	0.408	0.542	0.670	0.598	0.152	0.550	0.945
Mean	10–95	0.0238	0.0326	0.0407	0.0570	0.354	0.396	0.314	0.358	0.492	0.682	0.602	0.138	0.545	0.936

DRYING CURVES (508 = 1.00)

98	20.0	0.0265	0.0310	0.0370	0.049	.....	0.445	0.360	0.297	0.403	0.602	0.641	0.135	0.493	0.950
95	15.5	0.0258	0.0326	0.0370	0.0535	.....	0.431	0.387	0.330	0.440	0.658	0.658	0.149	0.545	0.955
90	12.95	0.0251	0.0324	0.0363	0.0548	.....	0.410	0.356	0.343	0.460	0.687	0.665	0.148	0.545	0.950
85	11.67	0.0238	0.0326	0.0364	0.0557	.....	0.407	0.348	0.343	0.461	0.694	0.646	0.148	0.548	0.945
80	10.65	0.0240	0.0320	0.0366	0.0565	.....	0.405	0.356	0.350	0.470	0.705	0.640	0.150	0.562	0.945
70	9.50	0.0234	0.0306	0.0366	0.0558	.....	0.394	0.361	0.354	0.477	0.702	0.635	0.153	0.557	0.943
60	8.54	0.0236	0.0310	0.0369	0.0554	.....	0.394	0.360	0.355	0.480	0.691	0.620	0.153	0.548	0.937
50	7.58	0.0238	0.0317	0.0369	0.0565	.....	0.391	0.360	0.356	0.484	0.675	0.600	0.154	0.533	0.930
35	6.17	0.0244	0.0317	0.0377	0.0577	.....	0.384	0.362	0.357	0.481	0.655	0.574	0.157	0.526	0.937
20	4.77	0.0266	0.0325	0.0388	0.0597	.....	0.376	0.360	0.369	0.475	0.655	0.566	0.161	0.523	0.947
10	3.74	0.0294	0.0337	0.0404	0.0613	.....	0.372	0.371	0.390	0.480	0.655	0.567	0.168	0.502	0.962
5	2.83	0.0328	0.0417	0.0465	0.0635	.....	0.409	0.399	0.399	0.480	0.643	0.594	0.176	0.498	0.955
Mean	10–95	0.0250	0.0321	0.0374	0.0567	.....	0.396	0.362	0.355	0.471	0.678	0.617	0.154	0.539	0.945

The soil surfaces have been calculated from the data in figure 1, assuming the particles to be spherical in shape. The assumptions which were made in

TABLE 5

Comparison of soil surfaces found by mechanical analysis and calculated from vapor-pressure data

SOIL NUMBER	TOTAL SURFACE PER GM.		SURFACE OF PARTICLES LARGER THAN						SURFACE OF PARTICLES >0.1 μ + TOTAL SURFACE
			0.1 micron radius			0.25 micron radius			
	Found	Calculated	Part disregarded	Found	Calculated	Part disregarded	Found	Calculated	
	sq. meters	*sq. meters*	*per cent*	*sq. meters*	*sq. meters*	*per cent*	*sq. meters*	*sq. meters*	
Trenton series									
S5	0.69	1.10	1.1	0.117	0.163	2.1	0.064	0.086	0.170
S7	0.77	1.52	1.5	0.141	0.226	2.2	0.107	0.129	0.183
S9	1.20	2.59	2.0	0.300	0.384	3.6	0.184	0.203	0.250
S12	3.14	5.20	6.6	0.578	0.606	9.9	0.340	0.408	0.184
S13	4.30	6.33	8.3	0.826	0.955	13.8	0.449	0.505	0.192
S14	4.36	7.10	8.6	0.930	1.075	14.2	0.526	0.570	0.212
S15	4.61	8.12	9.5	1.17	1.23	19.2	0.638	0.649	0.254
S16	8.34	9.45	17.6	1.45	1.42	27.5	0.720	0.750	0.174
S18	10.4	10.6	23.0	1.57	1.58	33.5	0.810	0.835	0.151
T5	1.36	2.93	0	1.36	0.435	0	1.36	0.230	1.00
T6	15.8	19.8	32.0	3.30	2.94	61.2	1.23	1.56	0.209
T7	24.8	26.0	56.0	3.02	3.86	92.0	0.251	2.04	0.122
993	6.82	8.77*	13.0	0.881	1.30*	17.2	0.579	0.69*	0.129
994	9.43	9.45*	19.2	1.117	1.40*	26.8	0.675	0.74*	0.120
T1	11.1	(11.1)	22.1	1.65	(1.65)	33.1	0.872	(0.872)	0.149
Abbott series									
SW5	0.0380	0.16	0	0.0380	0.046	0	0.0380	0.026	1.00
SW6	0.0458	0.21	0	0.0458	0.061	0	0.0458	0.035	1.00
SW7	0.0569	0.25	0	0.0569	0.075	0	0.0569	0.041	1.00
SW9	0.0884	0.37	0	0.0884	0.112	0	0.0884	0.063	1.00
G1	1.94	2.31	3.0	0.620	0.685	6.4	0.384	0.389	0.320
W.L.	3.59	2.59	7.3	0.628	0.77	10.7	0.375	0.435	0.175
B5	1.26	2.21	2.3	0.420	0.655	4.6	0.266	0.370	0.333
168	0.976	2.32	1.2	0.442	0.69	2.0	0.395	0.403	0.453
169	1.36	3.15	2.0	0.644	0.93	4.3	0.481	0.530	0.473
170	2.78	4.45	4.0	1.12	1.32	10.3	0.709	0.748	0.403
172	4.11	3.98	6.8	1.26	1.18	16.0	0.647	0.670	0.307
629	0.886	0.95	1.4	0.218	0.283	2.3	0.157	0.160	0.408
631	4.16	3.54	9.1	1.005	1.05	18.5	0.337	0.579	0.250
507	4.28	6.15	5.6	1.78	1.82	15.5	1.17	0.103	0.415
508	6.54	(6.54)	10.7	1.94	(1.94)	23.5	1.10	(1.10)	0.297

* Calculated by using ratios of vapor-pressure curves on isobars above 95 per cent.

estimating the size of the particles in the mechanical analysis have been discussed elsewhere (11). The principal uncertainty in the evaluation of the total surface is probably involved in the extrapolation of the distribution

curves. The results are given in table 5. The total surfaces have also been calculated by multiplying the values found for Trenton clay and 508, by the ratios of the vapor-pressure curves given in tables 3 and 4. The theoretical quantities are generally considerably larger than those determined experimentally.

Similar calculations have been made of the surface of the particles larger than 0.1 micron and also 0.25 micron radius, disregarding completely the smaller material in each case. As the amount of soil surface considered increases, the ratio of the theoretical to the actual surface increases. Except in unusual soils, this ratio becomes unity when the comparison is made on the basis of the particles larger than a dimension between these limits. This applies even to soils 170 and 172, in which case the heavier soil exhibits the lower hygroscopicity except at high vapor pressure. With the Trenton separates, more surface must be compared: the experimental values for the surface larger than 0.05 micron, in T6 and T7, are 5.27 and 6.48 square meters per gram, while the calculated values are 5.10 and 6.70, respectively. T5 requires the consideration of the surface of Trenton clay down to 0.02 micron.

Since it is really the smaller material which is responsible for most of the absorption, the relationships in table 5 must mean that the absorptive surface is usually more efficient in the lighter soils. The fact that these conditions obtain with substances of different chemical composition as well as with chemically related soils may be interpreted to indicate that the absorption is influenced mainly by the size and arrangement of the particles.

THICKNESS OF THE WATER FILM

The thickness of the water film deduced from the data in this paper ranges from molecular dimensions (about 5×10^{-7} mm.) at 1 per cent vapor pressure to about 2×10^{-5} at 98 per cent. These values are of the same order of magnitude as those found by Odén (14). Unless the estimated surface of the soil is too small it may be stated, contradicting the theory of Rodewald and Mitscherlich, that the water film is at least one molecule thick in an atmosphere of 1 per cent humidity instead of 96 per cent, as the "hygroscopicity" theory demands.

The following is suggested as the mechanism of adding water to an oven-dried soil. The first layer of water molecules is held so tenaciously that its vapor pressure is very low. A few succeeding layers cause greater increments of the vapor pressure and produce the part of the curve which is concave upward. Then the addition of more water results in a large increase in vapor pressure and the straight portions of the curves are obtained. The capillary spaces are probably commencing to fill at this stage. Finally, as the water wedges grow in size, it requires larger amounts of moisture to produce a given increment of the vapor pressure, and the curves are concave downward.

Table 5 seems to show that the relative power for absorbing water in a comprehensive series of soils is measured by the relative surfaces of the particles larger than 0.1 to 0.25 micron radius, independently of the smaller colloidal material, whereas it is really the latter which is responsible for most of the absorption.

This condition can probably be explained by the concept of the colloid-coated particle, such as has been postulated by Keen (12) to explain evaporation phenomena and by Comber (5, 6) to explain flocculation phenomena. On this view, the soil grains are enlarged by being coated with a jelly-like covering of colloidal material which collapses on drying to form a layer difficultly permeable to water, with a moisture gradient from the core to the outside. The total amount of water associated with this aggregate is therefore less than if its component particles were completely dispersed. Thick coatings would show these effects more noticeably than thin coverings, as is indicated by the two families of curves. The colloidal structure is partially destroyed by dehydration, and the coating becomes to some extent in effect a part of the core. This condition is slowly reversed by the addition of water, the speed and extent of the reversal depending upon the amount of water added. It may be remarked in this connection that in carrying out the mechanical analysis, when suspensions are evaporated which contain particles of low colloidal dimensions only, this material adheres to the weighing bottles as a vitreous mass which can not be removed without the greatest difficulty, whereas if coarser grains are also present in the suspension the weighing bottles can be easily cleaned.

This theory also explains the behavior of the soil in the mechanical analysis. In our method (11) and also in that of Odén (15) only one sedimentation is made. Accordingly, if the dispersion in the suspension is not complete at the start the results will indicate a coarser texture in the soil than really exists. The data given in the insert of chart C, figure 1 show that the soil samples did not always remain in contact with the deflocculating solution long enough (one or two days) to effect complete dispersion before the sedimentation commenced. This was invariably the case if the soil samples had been thoroughly air-dried or oven-dried. This error would not affect those methods which employ repeated gravity sedimentations because the colloids would be eventually peptized, but it might influence the more rapid centrifugal methods.

SUMMARY

The vapor-pressure-moisture curves of a comprehensive series of soils ranging from fine sands to tight clays and from highly calcareous to highly silicious materials have been investigated at comparatively low moisture contents, with special reference to the influence on the curves of wetting and drying the soils. Complete chemical and mechanical analyses have been made on these materials. It has been shown that:

1. The dynamic and static methods of measuring vapor pressure give identical results.

2. The chemical composition of these soils, which are generally deficient in organic matter, is a minor factor in its influence on the absorption of water.

3. The vapor-pressure-moisture function depends on the previous history of the soil. Drying is particularly effective in raising the vapor pressure at a given moisture content, the extent of this action depending on the completeness of the drying. This effect is reversed by protracted contact with moderate amounts of water or shorter contact with excess of water. The mechanical analysis also indicates that drying the soil makes the texture appear coarser.

4. If comparable vapor-pressure-moisture curves are considered all the soils may be divided into two groups, in each of which the relative amounts of hygroscopic water remain nearly constant over the range from 10 to 95 per cent of the vapor pressure of water. Changes in the slope and position of the curves due to wetting and drying treatments do not change the relative hygroscopicities. The existence of the two families of curves is probably accounted for by the relative amounts of colloidal and silty material.

5. These ratios of the hygroscopic water agree closely with the ratios of the surfaces, as determined by mechanical analysis, of the particles larger than about 0.1 to 0.25 micron radius, disregarding the smaller material.

6. The thickness of the moisture film agrees well with the corresponding value calculated from Odén's data (14) but is much smaller than the value found by Patten and Gallagher (16). The theory underlying the method of Rodewald and Mitscherlich (17) for estimating the total surface of a soil from the "hygroscopicity" is not confirmed.

7. The vapor-pressure-moisture function will probably furnish a means of studying the influence of soluble salts on the structure of soils.

8. The experimental data in this paper seem to confirm the theory of the colloid-coated particle developed by Keen (12) and Comber (5, 6).

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EXPERIMENTS WITH BACTERIAL SOIL FERTILIZING PREPARATIONS

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Soil inoculation came as a result of purely empirical observations, long before the discovery of the nodule microbe (*Bacillus radicicola*), and furnished a foundation for bacterial soil fertilizing preparations.

A German farmer *August Salfeld* (16), who was forced to cultivate an infertile soil, for the growth of legumes, conceived the thought of "manuring" with soil from fields which had produced good harvests of the same plants. The results were satisfactory and this original way of fertilizing became rather widespread in Germany, Holland, Denmark and other countries; at times this method gave even better results than saltpeter applications. At first the beneficial effects were attributed to the organic material of the added soil, but after the discovery of the nodule microbe by Hellrigel and Wilfarth (6), it was clear that they were due to an infection of *Bacillus radicicola*. Later Nobbe and Hiltner (15) suggested soil inoculation with pure cultures of the nodule microbes. Thus the first bacterial soil fertilizer, Nitragin, was introduced. It was cultures of *Bacillus radicicola* grown on gelatin. Cultures were prepared at the chemical plant in Höchst for clover, alfalfa, lupine, vetch and other legumes.

The first experiments with this fertilizer gave variable results. Nevertheless the inventors of Nitragin persevered and the study of its merits was transferred to the laboratory. The failures were at first attributed to the artificial environment of the microbes and to the excretions of the germinating seeds.

In view of this, Hiltner and Störmer (8) prepared "Nitragin" in the form of pure cultures of *Bacillus radicicola* in a liquid medium. The medium consisted of a 2 per cent peptone solution or skimmed milk.

Extensive experiments with this preparation in Bavaria gave very good results, only 17 per cent of the experiments having been negative. These experiments attracted the attention of investigators throughout the world. In England Bottomley (1) devised a preparation known as "Nitrobacterin." In America Moore (14) prepared "Nitroculture."

Bottomley conducted field experiments in England; the results were fairly good; he obtained increases of 25–50 per cent; only 20 per cent of the experi-

[1] Translated from the Russian by Jacob S. Joffe, New Jersey Agricultural Experiment Stations.

ments were a failure. Moore's "Nitroculture" was tested out in the United States on a much larger scale; about 2500 experiments were conducted in the different states. The experiments gave quite favorable results. Crop increases were obtained of 20–80 per cent. About 24 per cent of all the experiments were unsuccessful. Simultaneously experiments were set up by Vogel (20) in Europe and in Africa; about 5220 preparations were tried; all the experiments gave good results. Hiltner (7) organized in Germany about 300 experiments, 70 per cent of which were successful. Stutzer (19) obtained good results in 75 experiments out of 100. The underlying principles were not understood and the results obtained were purely empirical. The point of view of the investigators was that soil inoculation depends chiefly upon the quality of the preparation and preserving the vitality and activity of the bacteria. The sponsor of this view was Simon (18) who originated "Azotogen," a culture of *Bacillus radicicola* in a sterile soil, manured with lime. All the efforts of the investigators at that time were directed toward technical perfection of the preparations and the methods of application.

Kühn (13) prepared "solid Nitragin" consisting of cultures of *Bacillus radicicola* in sterile soil. Experiments with these fertilizers conducted by Feilitzen (4) on peat soil gave favorable results.

Experiments conducted by the author with the same preparations in vessels with peat soils, manured with lime, Thomas slag and potassium salts gave equally good results. Nevertheless, "Azotogen" and "solid Nitragin Kühn," even when of good quality and freshly prepared, had some defects; they did not represent pure cultures of *Bacillus radicicola* and dried out very quickly.

The next, most interesting point in the history of the application of bacterial soil fertilizers, pertained to the question of the need for bacterial inoculation of soils, that normally contain nodule microbes. The investigations of Duggar and Proucha (2) in a way answer this question. They have shown that *Bacillus radicicola* inoculated in sterile soil multiplies intensively; on the other hand, when this same sterile soil is mixed with non sterile soil, the propagation of the microbe slackens in proportion to the quantity of the added non-sterile soil. These experiments thus indicate that the nodule microbes under natural conditions cannot compete with other soil bacteria, progressively dying out and decreasing in numbers. This has been confirmed by Kalantarov (9). The author has also noted the rapid disappearance of the nodule microbes in the soil after harvesting legumes. It is easy to isolate nodule microbes from such a soil by using a medium specific for *Bacillus radicicola*, namely dextrose agar. The organism develops in characteristic ductile colonies similar to drops of wax, entirely different from the colonies of other microbes, which grow but in a very limited way in this specific medium.

The failure of the nodule microbes to compete with the typical soil bacteria depends, so to say, upon their parasitic existence on the plants, and therefore the soil is not a normal medium for them.

Direct observations on the growth of legumes show that under ordinary

conditions there may be the complete disappearance of the nodule microbes from the soil and consequently the growth of legumes without nodules. An acid reaction of the soils in the northern, north western and north eastern districts of Russia inhibits nodulation of legumes there. Investigations made on the root system of legumes in some parts of the Porchovsky district, government of Pskov, showed at times that even in the case of good harvests,

TABLE 1

Effect of various forms of inoculants on growth of legumes in sand cultures

TREATMENT	WEIGHT OF AIR-DRIED PLANTS			
	Clover		Vetch	
	Duplicate determinations	Average	Duplicate determinations	Average
	gm.	*gm.*	*gm.*	*gm.*
Control nitrates	23.3 21.6	22.45	25.22 20.91	23.05
Control without nitrate	2.7 1.8	2.25	2.9 2.1	2.5
Pure cultures of *B. radicicola*	17.00 14.30	16.05	18.9 13.87	16.38
Azotogen	13.8 11.2	12.5	15.6 12.4	14.0
Nitragin	12.1 8.9	10.5	13.2 8.87	11.0
Nodules	10.2 6.7	8.45	11.5 0.0	11.5

the nodules were absent, or present in such small numbers that they could not be of any significance to the plants. The roots have a weak development and one must conclude that in such cases the legumes draw their nitrogen not from the atmosphere, but from the soil; that is, instead of enriching, they exhaust the soil of its nitrogen. If we consider the enormous extent of such acid soils in Russia, it is easy to imagine the yield losses.

The experiments of Gerlach and, Vogel (5), Alfred Koch (11, 12), West (21) and others give but indirect information as to the conditions favoring the nitrogen-fixing bacteria: sufficient mellowing of the soil, fertilization with organic substances, which serve as a source of energy for the nitrogen fixing organisms, liming, etc.

TABLE 2

Comparison of crop yields on inoculated and uninoculated plots

EXPERIMENT NUMBER	NAME OF EXPERIMENTER AND PLANTS USED	SOIL	FERTILIZERS* PER DESIATINA†					CROP PER PLOT		INCREASE OF CROP
			Superphosphate	Thomas slag	K_2SO_4	CaO	Size of plot	Control	Inoculated	
			poods†	*poods*	*poods*	*poods*	*acres*	*poods*	*poods*	*per cent*
	Zhicharewa:									
1	Vetch	Tzernozeme mixed with clay	....	..	....	....	0.8	72	95	31.9
2	Vetch		....	..	....	50	0.8	72	87.5	21.5
3	Vetch	Podzol sandy loam, swampy	....	24	12	....	0.8	138	288	108.7
	Lashkewitch:									
4	Vetch	Podzol sandy loam, swampy	....	34	24	....	0.8	104	186	78.8
5	Vetch		....	34	24	....	0.8	141	193	37
	Shtokman:									
6	Vetch	Sandy loam and loamy sand	....	24	....	....	0.8	75	90	20
	Petrovsky:									
7	Clover	Sandy loam with loamy subsoil	....	24	12	150	2.7	196	256	30.6
8	Clover		....	24	12	....	2.7	208	204	....
9	Clover		....	..	....	....	2.7	144	184	27.8
10	Vetch		....	..	....	....	2.7	71	127	78.6
11	Vetch		....	24	12	....	2.7	108	131	21.3
12	Vetch		....	24	12	150	2.7	172	191	11
	Gloushkoff:						*sq. meters*	*pounds*	*pounds*	
13	Clover	Podzol sandy loam with red clay subsoil	....	..	....	....	38.3	30	40	33.3
14	Clover		....	24	....	....	38.3	31	43	38.3
15	Clover		....	..	....	100	38.3	32	41	28.0
16	Vetch		....	..	....	....	38.3	35	43	23.0
17	Vetch		24	..	....	....	38.3	37	48	29.7
18	Vetch		....	..	....	100	38.3	35	48	37.0

	Pissareff:									
19	Vetch	Sandy loam poor in humus	....	..	....	180	4.8	11.22	14.0	24.0
20	Vetch		....	..	....	180	4.8	13.0	14.15	9.4
	Stahl:						*acres*	*poods*	*poods*	
21	Vetch	Loamy sand	22.5	..	13.5	....	2.7	640	682	6.5
22	Vetch	Sandy loam	22.5	..	13.5	....	2.7	630	718	14
23	Clover		22.5	..	13.5	....	2.7	536	546	....
24	Clover		22.5	..	13.5	....	2.7	570	514	....
25	Vetch		....	24	....	....	2.7	424	518	22.1
26	Vetch		....	24	....	....	2.7	376	484	28.7
	Engelgard Exp. St.						*sq. meters*	*pounds*	*pounds*	
27	Vetch	Sandy loam with forest litter	....	..	....	....	24.6	16.4	25.6	56.1
28	Vetch		....	..	....	....	24.6	21.7	27.0	30.4
29	Vetch		....	..	....	....	24.6	18.2	24.4	34.0
30	Vetch		....	..	....	....	24.6	18.7	19.0	....
31	Vetch		3	..	....	....	24.6	29.8	29.9	....
32	Vetch		3	..	....	....	24.6	19.7	26.7	35.5
33	Vetch		4	..	4	....	24.6	26.5	31.0	17.0
34	Vetch		4	..	4	....	24.6	25.8	29.5	14.3
35	Vetch		....	..	....	....	24.6	29.7	38.4	29.3
								gm.	*gm*	
36‡	Vetch	1.8 gm. Na_3PO_4	....	..	....	....	....	40.05	51.3	28.2
37‡	Vetch		....	..	0.48 gm.K	....	....	40.15	44.8	11.6
	Allen:						*acres*	*poods*	*poods*	
38	Vetch	Sandy loam	....	..	....	....	0.5	41	50.7	23.7

* Nitrogenous fertilizers were used in experiment 3 in the form of $(NH_4)^2SO_4$ (32 kgm. per acre) and in experiments 7, 12, 51 and 53 in the form of $NaNO_3$ (32 kgm. per acre).

† Pood = 16.38 kgm.; one Russian pound = 0.41 kgm.; desiatina = 2.7 acres.

‡ Experiments conducted in pots.

TABLE 2—*Continued*

EXPERIMENT NUMBER	NAME OF EXPERIMENTOR AND PLANTS USED	SOIL	FERTILIZERS* PER DESIATINA†					CROP PER PLOT		INCREASE OF CROP
			Superphosphate	Thomas slag	K_2SO_4	CaO	Size of plot	Control	Inoculated	
			poods†	*poods*	*poods*	*poods*	*acres*	*poods*	*poods*	*per cent*
	Benevolensky:									
39	Vetch, Oats	Slightly decomposed peat soil with a high ash content	....	24	15	....	1.0	390	438	12.3
40	Vetch, Oats		....	24	15	....	0.4	270	348	25.2
	Reineck:						*sq. meters*	*pounds*	*pounds*	
41	Clover	Virgin clay	....	..	....	....	28.7	187	205.5	10.0
42	Clover		24	..	12	....	28.7	....	216.3	29.3
43	Clover	Old neglected hot beds, not used	....	..	....	....	4.8	No account of the crop was was made. The plant on the inoculated plots seemed denser		
44	Vetch		....	..	....	....	4.8			
45	Lupine		....	..	....	....	4.8			
	Bachteeva:							*sheaves*§	*sheaves*	
46	Vetch	Drained peat bog	....	24	12	150	9.6	11.5	16.5	43.5
47	Clover		....	24	12	150	9.6	6.6	10.3	56.0
	Sawinoff:							*pounds*	*pounds*	
48	Clover	Drained peat bog	....	24	24‖	200	9.6	248	395	59.2
49	Vetch		....	24	24‖	200	9.6	480	500	....
	Makrinoff:									
50	Clover	Virgin sand	....	24	12	150	0.5	3/8	4/8	33.3
51	Clover		....	24	12	150	0.5	6/8	7/8	17
52	Vetch		....	24	12	150	0.5	1/2	3/4	50
53	Vetch		....	24	12	150	0.5	5/8	7/8	40

§ The crop was estimated by standard sheaves from 5 square meters.
‖ Wood ashes.

Thus, it may readily be seen that with out present knowledge the cardinal questions are:

1. What are the causes of failure of the bacterial soil fertilizers?
2. Can soil inoculation be used widely in our common farm practices?

These two questions led to the investigations reported here. Vessels of 5-kgm. capacity were filled with sand which had been previously ignited and washed with HCl. Knop's culture solution without saltpeter was used for all cultures except the controls which received also the saltpeter. The vessels after planting were kept in the greenhouse for 2.5 months. "Azotogen," "Nitragin Kuhn," nodules and pure cultures of *B. radicicola* prepared by the author were used in this experiment. Table 1 gives the plan and the results of the experiment.

TABLE 3

Effect of various treatments on number of nodules

EXPERIMENT NUMBER	PLANTS	TREATMENT	AVERAGE NUMBER OF NODULES ON FIVE ROOTS	
			Non-inoculated	Inoculated
16	Vetch	Without manure	27	47
13	Clover	Without manure	41	100
1	Vetch	Without manure	32.6	36.8
2	Clover	Without manure	45.4	81.8
2	Clover	Without manure	46.0	....
18	Vetch	Lime	36.0	52
15	Clover	Lime	58.0	108
3	Vetch	Lime	53.0	89
17	Vetch	Superphosphate	21.0	49
14	Clover	Thomas slag	58.0	98
3	Clover	Lime with liquid dung	50.4	112.2
3	Vetch	Lime with liquid dung	67.6	127.8

The preparations used in the sand cultures were then tried out in field experiments. The results were rather obscure. Many of the experiments proved the value of inoculation, while others did not.

The experiments were conducted in various parts of the country but unfortunately some of them, especially those in the war zone, were lost. In all the experiments an effort was made to supply calcium, phosphorus and potassium to the soil for the benefit of the nodule forming bacteria, avoiding acid phosphate, since it imparts temporarily an acid reaction to the soil. It is known that an acid reaction inhibits the development of nodule bacteria; even root excretions, usually of an acid nature, retard the growth of the nodule bacteria.

The results obtained may be summed up as follows:

1. Increase in crop yields, due to inoculation as presented in table 2.
2. Increase of the number of nodules on the inoculated plots as shown in table 3.
3. Increase in weight of roots of the infected plants.

Table 2 shows that generally the greatest success with inoculation was obtained with those experiments in which the alkaline manures were applied: Thomas slag, or lime, or both, as in experiments 3–8. Very instructive are experiments 21–26 made by Stahl. Here the application of acid manures on loamy soil (superphosphate, potassium salt in the experiments 21–24) gave no result whatever, on the contrary the application of Thomas slag on the same soil (experiments 25–26) showed at once a definite beneficial effect. The unfavorable results may be ascribed to the acid reaction of the northwestern and eastern soils of Russia on one hand and on the needs of calcium by the legume bacteria on the other hand. It may be inferred therefore, that experiments with soil inoculants without supplying calcium, phosphorus and potassium fertilizers of a neutral or alkaline reaction are bound to fail. For this reason probably the experiments of Severin (17) failed.

Table 2 also shows that in some cases (13–16, 27–30–32) favorable results were obtained even on those plots where no manures were added. Upon examination it was found that these plots were supplied with fertilizers in previous years.

The success of the soil inoculation without preliminary manuring with lime, phosphorus and potassium salts in western Europe may be explained by the superior cultivation of the soil.

Saltpeter manuring gave interesting effects. It is known that additions of saltpeter in artificial cultures has an unfavorable effect on the nitrogen fixing capacity of the microbes, reducing or completely suppressing it; the results in the field corroborated these observations. When the soil was treated with 6 poods of saltpeter per desiatina inoculation had no effect. The crop did not increase and the nodules did not appear on the roots. Figs. 3 and 4 represent roots from plots which did not receive saltpeter (exp. 50–52). Plate 1 represents roots from plots manured with saltpeter (exp. 51–53). The roots are bare, almost devoid of nodules and with thin ramifications.

These results corroborate in a way the work of Düggeli (3), who found that saltpeter inhibited the growth of azotobacter and decreased the numbers of them as compared with those plots which received no saltpeter. Table 3 shows the increase of nodules on the roots of infected plants in comparison with noninfected ones. It is well to record the fact that the increase in number of the nodules is even more constant than the increase in the crop.

This table also shows that the manuring with lime and Thomas slag had a beneficial action on nodulation. Manuring with superphosphate in certain experiments (exp. 17) the number of nodules was lowered even in comparison to the plots which had not received mineral manuring at all.

In summing up the work reported the following conclusions may be drawn:

1. A properly prepared inoculant applied properly to the soil and keeping the soil in condition for the proper development of these organisms, will in most cases be beneficial from the standpoint of inoculation.

2. The indispensable conditions for successful application of the preparation are: a mellow soil, proper moisture content and well selected fertilizers.

3. With the precautions noted, soil inoculation may be practiced on a large scale under field conditions.

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PLATE 1

FIG. 1. A TYPICAL ROOT OF VETCH FROM A PLOT, FERTILIZED WITH MINERALS WITHOUT NITRATES AND INOCULATED WITH NODULE BACTERIA

FIG. 2. A TYPICAL ROOT OF CLOVER FROM A PLOT, FERTILIZED WITH MINERALS WITHOUT NITRATES AND INOCULATED WITH NODULE BACTERIA

There were a great number of small nodules which the photograph does not show.

FIG. 3. A TYPICAL ROOT OF VETCH WHERE NITRATES WERE USED; NO NODULES ARE PRESENT EVEN THOUGH THE PLOTS WERE WELL INOCULATED

FIG. 4. A TYPICAL ROOT OF CLOVER, WHERE NITRATES WERE USED; NO NODULES ARE PRESENT, EVEN THOUGH THE PLOTS WERE WELL INOCULATED

FIG. 1

FIG. 2

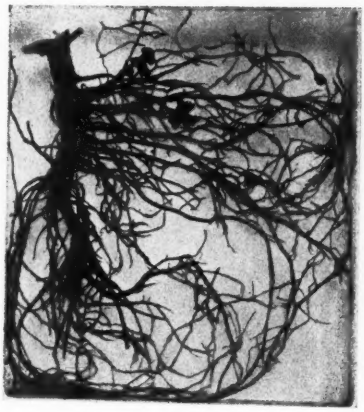

FIG. 3

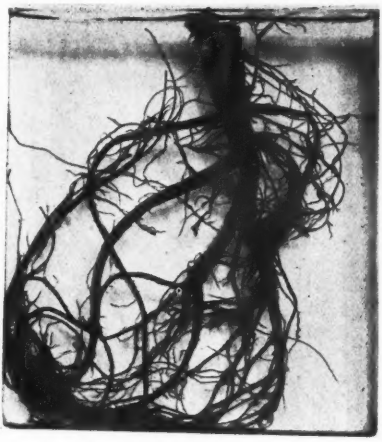

FIG. 4

IS IT POSSIBLE TO MAKE A BACTERIAL SOIL PREPARATION FOR NON-LEGUME CROPS?

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Soon after the introduction of nitragin, attempts were made to work out also a bacterial soil-fertilizing preparation for non-legumes. At first, it was thought, that the nodule microbes could be utilized, but experiments showed that infection of the crops with *Bacillus radicicola* gave no results whatever. Neither soil inoculation, nor infection of the seeds, nor even injection of the nodule microbe cultures into the stems, had any influence on the crops.

The failure to utilize the nitrogen-fixing organisms for all crops induced the search for a preparation of cultures of other microbes. It was expected that these preparations would intensify the bacterial processes in the soil which in turn would have a beneficial influence on the development of the plants. The question at once arises as to whether any one ever attained an intensification of these processes with the methods of inoculation practiced? The first preparation "Alinit" was introduced by a German landowner named Caron on his estate Ellenbach. He prepared a culture of an organism which is at times very abundant in the soil; it was named *Bacillus ellenbachensis*. The biochemical or physiological characters were not investigated.

Caron (3) had not even identified the species of the microbe, some investigators identified it as *B. megatherium* [Stoklasa (17)], others as *B. subtilis* [Lauck (10)], Severin (16) found two microbes in Alinit which he named *B. ellenbachensis*. Hartleb (7) regards this microbe as an independent species of the hay bacillus group. The biochemical behavior of the Alinit organisms was investigated by Stutzer and Hartleb (18) and they place them in the group of typical putrifying or ammonia-producing organisms. Besides the above microbes some preparations carried also nitrifying organisms, like that of Beddies (2). Lipman (11) conducted experiments inoculating the soil with various species of Azotobacter, but there was no increase of nitrogen in the soil or plants.

These preparations were tested out and in most cases the results were negative. It will suffice to mention the work of Lutoslawski (12), West (20), Gerlach and Vogel (5) and Koch (9). It has been shown that the ammonifying and nitrifying organisms carried in those preparations are present in the soil and therefore such preparations are of no value as inoculants. Attention must, however, be directed to the non-symbiotic nitrogen-fixing bacteria, such as *Clostridium pasteurianum* and Azotobacter. Düggeli (4) realized the importance of such studies and investigated the effect of various substances on the nitrogen fixing organisms.

It has been recognized that in some soils the nitrogen-fixing organisms are insufficiently

[1] Translated from the Russian by Jacob S. Joffe, New Jersey Agricultural Experiment Stations.

provided with carbonaceous matter. This impedes the process of nitrogen fixation, for the carbonaceous material is essential as a source of energy for these organisms. The store of soil nitrogen is thus more readily exhausted and the nitrogen problem becomes acute. In artificial cultures nitrogen fixation proceeds favorably when sugars, alcohols, calcium salts of organic substances, etc., are used. Under field conditions nearly all of these are absent from the soil. The question arises, what are the materials in the soil that are utilized as a source of energy by the nitrogen fixing organisms? Gerlach and Vogel (5) found that starch, cane sugar or mannitol were not used by the nitrogen fixing organisms and crop yields were depressed. Koch (9) attempted to explain the failure of Gerlach and Vogel. According to him the addition of the nutrients increases the microbial population in the soil to such an extent that they compete with the plants for food. The increase in crop yields should come in the second year, due to the decomposition of microbial bodies. He repeated the experiments and obtained an increase of yield amounting to nearly 250 per cent.

The source of carbon for the nitrogen fixing bacteria in the soil was not disclosed by these experiments, moreover the substances used in the experiments of Gerlach and Vogel could find no practical application. The investigations of Pringsheim (14) and Koch (9) seem to have solved the question. Three series of flasks were filled with a mineral solution for the nitrogen fixing bacteria; in the first series sugar was used as a source of carbon; in the second, mannitol; in the third, cellulose (Swedish filter paper). The first two series of flasks were inoculated with a pure culture of Azotobacter, the third with a mixture of aerobic cellulose bacteria and Azotobacter. After a certain period total nitrogen was determined by the Kjeldahl method. The results showed that the cultures inoculated with cellulose bacteria and Azotobacter gave the highest amount of nitrogen. It is known that the aerobic cellulose bacteria decompose cellulose, forming as intermediary products various organic acids. The calcium salts of these acids are a suitable source of carbon for the nitrogen-fixing bacteria. In the soil, great masses of vegetation are being decomposed by the cellulose bacteria, and the resulting products (organic salts of the alkali metals) may well serve as a source of carbon for the nitrogen-fixing bacteria. The above mentioned experiments also teach us the methods of microbiological operations for the stimulation of cellulose decomposition in soils rich in undecayed vegetative residues such as peat soil, soil after a good harvest of legumes, etc. One may expect, a priori, that the addition of cellulose bacteria and Azotobacter to such soils fertilized with mineral manures must exercise a favorable influence upon their fertility.

Makrinoff (13) has shown that the proper selection of mineral manures exerts a definite favorable influence on the legume bacteria. Such a selection must not only serve the needs of plants, but must also suit the physiological and biochemical peculiarities of the microbes used. The question arises: how should we fertilize a soil, rich in plant residues, when a mixture of cellulose bacteria and nitrogen fixing organisms is applied? The cellulose bacteria form, as intermediary products, organic acids whose calcium salts are utilized as sources of carbon for Azotobacter. For this reason the application of lime is an indispensable condition for success. Thomas slag, potassium salts, or

wood ashes are important. The first experiments were conducted on virgin peat soil; four plots were used, the first being the control plot; the other three received the following treatment:

250 poods[2] of lime per desiatina[3]
24 poods of Thomas slag per desiatina
24 poods of potassium salts per desiatina

The first two plots were not inoculated, the third plot was inoculated with nitrogen assimilating bacteria (Azotobacter), the fourth plot with a mixture of Azotobacter and aerobic cellulose bacteria as outlined by Van Iterson (19).

Cellulose bacteria could be cultivated in the following mineral solution:

	per cent
K_2HPO_4	0.5
$MgSO_4$	0.1
$(NH_4)MgPO_4$	2.0

To this solution 0.1 per cent of soil extract was added. The latter is made up as follows: a tzernozeme soil is treated with a 10-per cent HCl solution to remove various mineral substances; after 1 or 2 days digestion, the HCl is poured off, and the soil is washed with water until free from HCl. The soil is then digested with a 10-per cent ammonia solution for 1 or 2 days, the mixture being stirred frequently. The ammonia digest is poured off into a flat dish and evaporated on a steam bath. The residue is an ammoniacal salt of humic acid. The medium thus prepared was poured into "Kressling flasks." Filter paper made by Schleicher and Schühl was then added. Bacterial growth in the form of a yellow deposit appears at the surface after 24–48 hours. The filter paper becomes slimy and settles to the bottom. The yellow growth of the cellulose bacteria accumulates at the bottom and the filter paper dissolves rapidly. At that stage the cultures are rich in cellulose-destroying organisms, and Azotobacter is added. This preparation was used for sprinkling the seeds, oats having been used in the experiment.

The results of the experiment were as follows:

Plot 1. No crop could be harvested.
Plot 2. Crop weighed 16 pounds.[4]
Plot 3. Crop weighed 41 pounds, an increase of 156 per cent over plot 2.
Plot 4. Crop weighed 57 pounds, an increase of 257 per cent over plot 2.

Plate 1, figure 1 represents the standard sheaves from one square arshine[5] from plots 2, 3 and 4.

The second experiment, was conducted on a peat soil that had been under cultivation for a long time. The procedure followed was the same as in the

[2] Pood = 16.38 kgm.
[3] Desiatina = 2.7 acres.
[4] A Russian pound is 0.41 kgm.
[5] An arshine is equivalent to about one meter.

preceding experiment. The size of the plots was 18 square arshines. Plate 1, figure 2 shows representative sheaves. The data are as follows:

Plot 1. Crop weighed 54 pounds.
Plot 2. Crop weighed 67 pounds, increase of 24 per cent over plot 1.
Plot 3. Crop weighed 74 pounds, increase of 10.5 per cent over plot 2.
Plot 4. Crop weighed 94 pounds, increase of 40.3 per cent over plot 2.

Thus the mineral manuring gave crop increase of 24 per cent. Bacterial infection with nitrogen-fixing bacteria brought about an improvement of the crop equally only 10.5 per cent (over plot 2); cellulose bacteria supplemented with nitrogen-fixing Azotobacter led to the greatest increase of the crop equalling 40.3 per cent.

The vegetation on plot 4, infected with cellulose and nitrogen-fixing microbes, was particularly dense and vigorous in comparison with that on the other three plots. Plots 2 and 3 differed little. The roots and stems on the infected plots 3 and 4 were better developed than on plots 1 and 2. The average lengths of stem at the time of harvest were:

	cm.		cm.
Plot 1	95	Plot 3	105
Plot 2	105	Plot 4	116

Plate 2 shows the roots and stems of representative plants on the different plots.

In these experiments only the crops from the three plots infected with Azotobacter attract our attention. It is usually assumed that Azotobacter is not capable of influencing the crops; nevertheless the third plot in the first experiment showed a crop increase over that of plot 2 of more than 150 per cent. This result may be explained by the presence of cellulose bacteria in the peat soil. This same plot in the second experiment showed only an insignificant increase. The difference may be explained by the differences in the composition and structure of the soil.

In the first experiment the soil was represented by a considerable depth of peat, the upper layer of which had a spongy structure; the second experiment was made on a cultivated soil acid in reaction and whose organic matter was in an advanced stage of decomposition. In this soil the cellulose bacteria had probably disappeared.

Similar experiments were made on the swampy experimental field of Novogord, at the Pechersky Agricultural Station and elsewhere. The arrangement and treatment of the plots were the same as in the preceding experiments. The plan and results are given in table 1.

The vetch shows an increase in yield; the clover also gave a visible increase; as for the oats there was a decrease.

In experiment 8 some effect of bacterial infection even where no lime was used was obtained thanks to the rather high proportion of lime in this black soil, which also has a limestone subsoil.

The above experiments were made in years 1915–16. Only in 1917 a communication was received concerning the experiments of Bottomley (1) with "bacterized peat." His experiments involved the mixing of ground peat with lime and Thomas slag, and infecting it with "humate" which probably means cellulose bacteria. After two or three weeks he sterilized the peat with steam and infected it with Azotobacter.

TABLE 1

The influence of inoculation with cellulose and nitrogen fixing bacteria

PLANTS AND LOCALITY OF EXPERIMENT	FERTILIZERS USED PER DESIATINA*				YIELDS PER PLOT					
	Superphosphate	Thomas slag	K_2SO_4	CaO	Plot 1 (control)	Plot 2 (minerals without inoculation)	Plot 3 (minerals and Azotobacter)		Plot 4 (Minerals, Azotobacter, and cellulose bacteria)	
							Yield	Increase over plot 2	Yield	Increase over plot 2
	poods†	*poods*	*poods*	*poods*	*pounds*‡	*pounds*	*pounds*	*per cent*	*pounds*	*per cent*
Novorgorod Experiment Station										
1. Vetch	..	24	12	150	1.0	11.5	16.5	43.5	16.5	43.5
2. Clover	..	24	12	150	5.9	6.6	7.2	9.1	10.3	56.0
3. Timothy	..	24	12	150	10.0	28.0	31.0	10.7	29.0	3.5
4. Oats	..	24	12	150	4.2	4.2	4.2	0.0	2.8	....
5. Oats	..	24	12§	200	There was more vigorous growth on the inoculated plots					
Pecherskaya Experiment Station										
6. Barley	..	31	24	150	....	7.5	10.5	40.0	10.25	36.6
7. Barley	20	..	24	150	....	9.75	8.9	....	17.9	83.6
Yeletz Experiment Station										
8. Oats	..	..	..	...	....	3.46	....	....	4.20	21.4

* Desiatina = 2.7 acres.

† Pood = 16.38 kgm.

‡ Russian pound = 0.41 kgm.

§ Wood ashes were used in place of potassium fertilizers.

These experiments have a certain analogy to the field experiments described here.

The proposed treatment of soils rich in organic residues, is based on the possible acceleration of decay of such inert and difficultly decomposable materials. By this process it is possible to avoid carbonization and humification of soils rich in organic matter.

Hall (6) recommends mineral manuring with saltpeter, phosphorus and potassium for peat soil. The above described method of manuring is more

advantageous inasmuch as the cellulose bacteria are effective in decomposing the organic residues, and besides, the nitrogen accumulation is important.

The above described experiments must be regarded as preliminary. The work is being continued on a large scale and the results will be published in the near future.

CONCLUSION

Bacterial inoculation and soil cultivation and fertilization must not only strictly correspond to the needs of plants, but also to the physiological requirements of the microbe employed.

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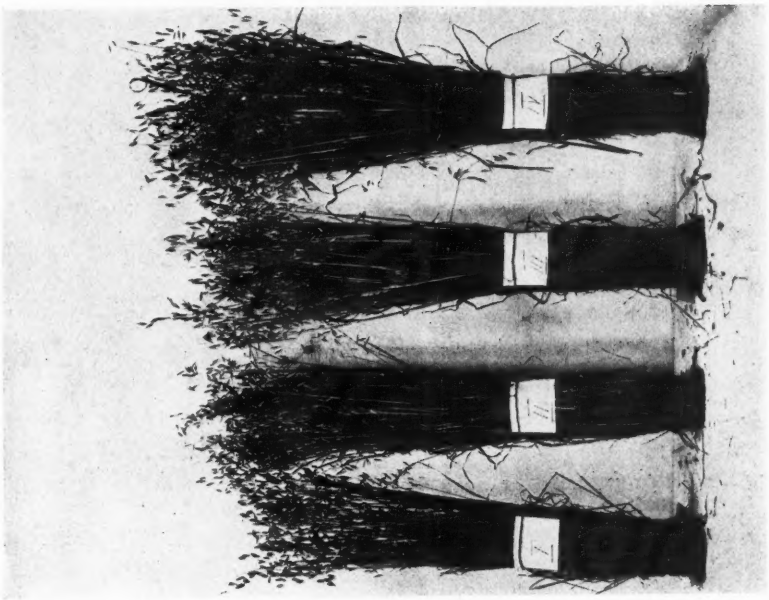
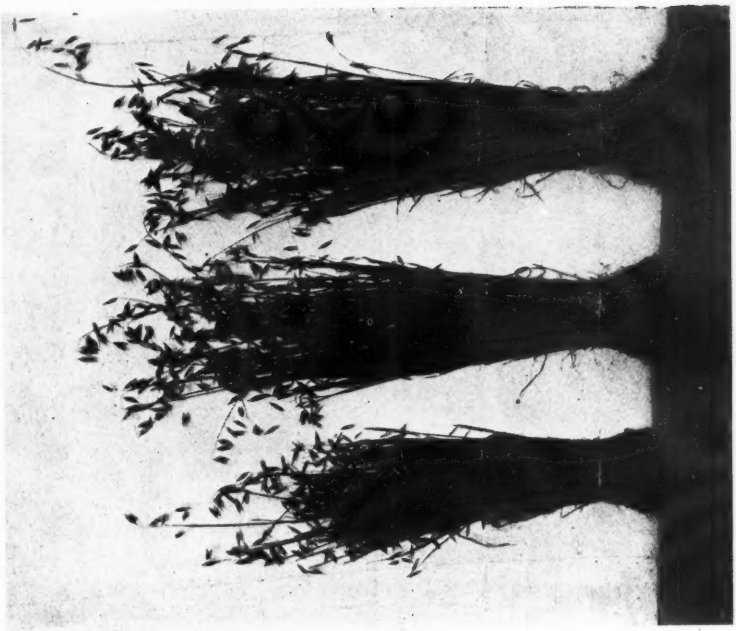
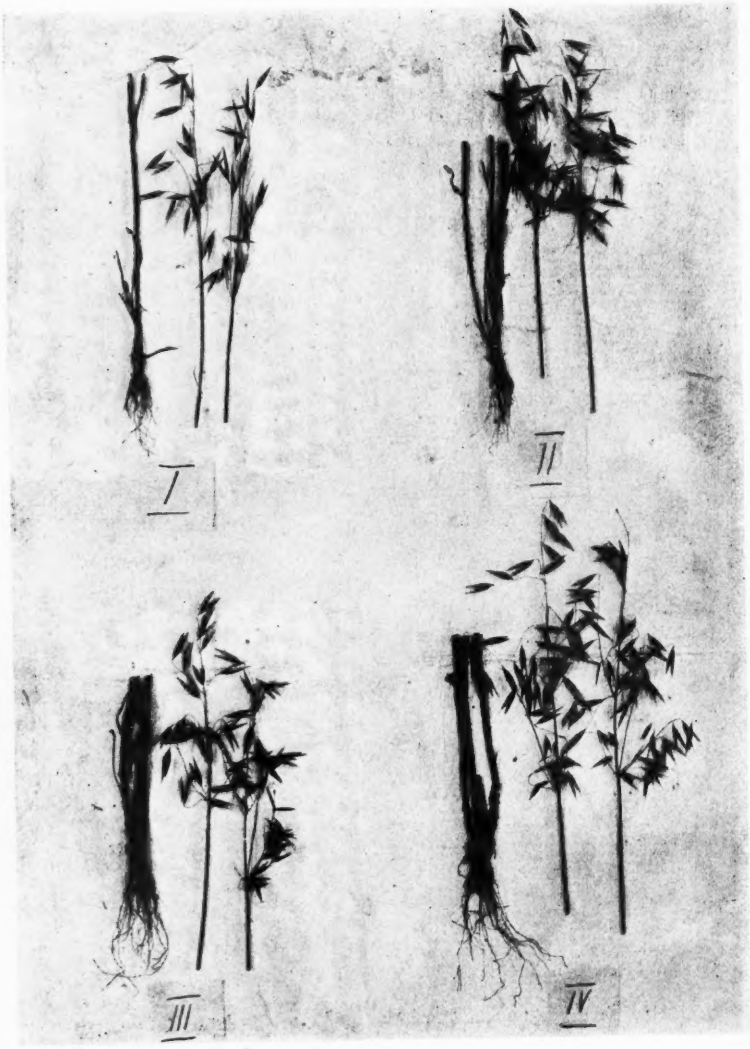


FIG. 2



Plot 2 Plot 3 Plot 4

FIG. 1


I
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III
IV

RELATIVE AVAILABILITY OF THE PHOSPHORUS OF RAW ROCK AND ACID PHOSPHATE IN SOILS

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INTRODUCTION

It is a mooted question among soil workers whether acid phosphate or rock phosphate is the better and the more economical source of phosphorus for crop production and the maintenance of soil fertility. Notwithstanding the great amount of work on this problem that has been done in various parts of the world, the question is far from being solved.

The results of investigations reported are often conflicting and sometimes not strictly comparable. It was thought advisable, therefore, to compare these two forms of phosphatic fertilizers in their behavior after they are applied to various types of soil, and also to study some of the factors that influence their behavior.

It would be of fundamental importance to know: What becomes of the phosphorus when phosphatic fertilizer is applied to the soil? What reactions take place? To what extent is phosphorus "available" when "water soluble" acid phosphate is incorporated with the moist soil mass?

As is generally known, one of the strongest claims of acid phosphate advocates is that acid phosphate is water soluble and that when it is applied to the soil, phosphorus becomes immediately available for the use of plants, while phosphorus in rock phosphate is so insoluble that its availability is too low for the immediate use of growing crops. The validity of this contention is often doubted, for it has been observed that the phosphorus of water soluble acid phosphate could not be extracted from the soil to which it was previously added. It is often argued, however, that although this phosphorus can not be extracted with water, it is absorbed or even adsorbed by the soil particles and loosely held thereby. This phosphorus, it is further claimed, is in such state that plant roots are able to extract it far more easily then the phosphorus of insoluble rock phosphate. The data presented in this paper will tend to show that this general contention is also of questionable validity; that the phosphorus of acid phosphate or even of double acid phosphate (superphosphate) after this material is applied to some agricultural soils, becomes very insoluble; and that its solubility is not to any extent greater than the solubility of phosphorus from rock phosphate added to the same soil, under the same conditions.

EXPERIMENTAL

The present investigation was carried out on many soil types, the soils in the majority of cases being obtained from Champaign county, Illinois. The phosphatic fertilizers used were three different rock phosphates, five slags, ground apatite, iron and aluminum phosphates, steamed bone meal and acid and double acid phosphates. The composition of these phosphatic fertilizers is presented in table 1.

The comparative work on different soils was carried out with Tennessee rock phosphate as a representative of insoluble rock phosphate, and with double acid phosphate as an easily soluble phosphatic fertilizer.

TABLE 1

Phosphorus content of phosphatic fertilizers used

FERTILIZER	PHOSPHORUS	AMOUNT OF MATERIAL CONTAINING 4 MGM. OF PHOSPHORUS
	per cent	*gm.*
Tennessee rock phosphate	13.8	0.0290
Double acid phosphate	19.94	0.0201
Slag A	8.40	0.0476
Slag B	9.30	0.0430
Slag C	5.79	0.0691
Slag D	6.61	0.0605
Birmingham slag	8.55	0.0468
Blue rock	13.05	0.0306
Florida soft rock	14.77	0.0271
Apatite	12.36	0.0324
Iron phosphate	16.36	0.0244
Aluminum phosphate	17.09	0.0234
Acid phosphate	9.54	0.0419
Steamed bone meal	14.81	0.0270

The general procedure of the experiment was as follows:

Twenty-five grams of mineral soil or 12.5 gm. of organic soil (peat) was placed in a 350-cc. glass bottle, thoroughly mixed with a given amount of fertilizing material, moistened with distilled water, and allowed to stand for seven days at room temperature. At the end of this period, this mixture was shaken with 250 cc. of 0.2 *N* nitric acid for three hours in a shaking machine. Then it was filtered on a dry filter paper. A 200-cc. aliquot of clear solution was taken for determination of phosphorus. The volumetric method of analysis was followed in this work. The tables show averages of two determinations.

It is often recommended that acids sufficiently stronger than one-fifth normal be used in studies of weak acid extractions so that after the soil bases are neutralized, the remaining acidity will be equal to one-fifth normal. Such an arrangement, of course, would give the phosphatic compounds in different soils the same chance for equal solubility. This procedure, however, introduces a very objectionable feature for the comparative study of different soils. The solvent would necessarily be different for nearly every soil, and the

results could hardly be comparable. It seems as though we should accept soils as such; accept the conditions under which any given soil has to function, and make our observations, preserving these conditions intact.

Suppose there are given two soils; one is abundantly supplied with carbonates, while the other is very deficient in them. The acids formed in the soils will be used largely to neutralize the carbonates in the first soil, and will be available as free acids in the second soil. Naturally there will be more phosphorus available for crops in the second soil than in the first. The field observations at various experiment stations show that soils excessively supplied with lime do not respond very well to the application of phosphates. This well known fact among soil workers seems to justify the procedure here adopted.

In time, the biological activities of these soils will also add to the modification of their soil solution, but this phase of the problem does not enter into the realm of the present study.

BEHAVIOR OF PHOSPHORUS APPLIED TO DIFFERENT SOILS

The work was done on soils of different geological and morphological formations. Prairie soils were represented by three samples of brown silt loam; two of black clay loam; one each of drab clay loam, brown gray silt loam on tight clay, and brown sandy loam. Timber soils were represented by one sample each of yellow gray silt loam on gravel, yellow silt loam eroded and yellow gray sandy loam. Terrace soils were represented by brown sandy loam. Mixed loam was used as a bottom land type formed along rivers. Deep peat was a representative of swamp lands.

In each soil type the soils of three different depths were used for the comparative tests with the phosphatic fertilizers: (a) the plowed layer of $6\frac{2}{3}$ inches in depth, (b) the layer from $6\frac{2}{3}$ to 20 inches, and (c) the layer from 20 to 40 inches. These strata will be designated as surface, subsurface and subsoil, respectively. The second and the third layers, of course, differ from the first one in their physical and chemical properties, and the descriptive name of soils for each layer is given here in order to facilitate interpretation of the data presented. All soils in this experiment were from stock samples, collected in 1915 in Champaign county for the soil survey analyses, air-dried and pulverized at the time. Since then, they were kept in 2-quart fruit jars. The soils of Champaign county are described in Illinois Agricultural Experiment Station Soil Report (1).

These fourteen soils of three layers each, or forty-two samples in all, were treated with either Tennessee rock phosphate or double acid phosphate in such amounts that in each case 4 mgm. of phosphorus were applied to 25 gm. of mineral soil and to 12.5 gm. of the first two layers of peat soil. The results presented in table 2 show the percent of applied phosphorus that was extracted with 0.2 *N* nitric acid. In each case the amount of phosphorus extracted from the untreated soil was subtracted from the amount of phosphorus ex-

TABLE 2

Phosphorus recovered from Tennessee rock phosphate and double acid phosphate

SAMPLE NO.*	SOIL SURVEY NUMBERS	SOIL DESCRIPTION BY LAYERS	RECOVERY OF PHOSPHORUS		DEVIATION		ALKALI REQUIRED PER 10 CC. EXTRACTED SOLUTION
			From rock phosphate	From double acid phosphate	+ or −	Squared	
			per cent	*per cent*			*cc.*
		Prairie soils					
		Brown silt loam:					
1	7729	Brown silt loam	45.5	48.3	−2.8	7.84	11.4
2	7730	Brown silt loam passing into yellow clayey silt	35.3	36.8	−1.5	2.25	11.4
3	7731	Yellow clayey silt with till	0.2	0.0	+0.2	0.04	0.2
		Brown silt loam:					
4	7741	Brown silt loam	55.2	61.5	−6.3	39.70	10.6
5	7742	Brown silt loam with some yellow	47.7	47.7	0.0	.....	10.7
6	7743	Yellow clayey silt with some brown	43.5	44.2	−0.7	0.49	11.3
		Brown silt loam:					
7	7765	Brown silt loam	50.2	49.2	+1.0	1.00	11.3
8	7766	Brown silt loam with some yellow	37.7	33.5	+4.2	17.64	11.2
9	7767	Yellow clayey silt, more silty with depth	42.5	41.5	+1.0	1.00	11.0
		Black clay loam:					
10	7840	Black clay loam to dark brown	66.3	65.8	+0.5	0.25	12.4
11	7841	Drab to black clay loam	66.0	64.5	+1.5	2.25	12.6
12	7842	Yellow to brownish yellow and drab clay	53.0	53.8	−0.8	0.64	11.9
		Black clay loam:					
13	7825	Black clay loam with some sand	58.0	55.7	+2.3	5.29	12.2
14	7826	Black clay loam, some gravel and sand	49.5	50.0	−0.5	0.25	12.1
15	7827	Drab to olive colored clayey silt	45.3	43.5	+1.8	3.24	11.8
		Drab clay loam:					
16	7843	Drab clay loam, dark	60.0	59.0	+1.0	1.00	10.0
17	7844	Drab clay loam, lighter at 12 in.	56.7	65.0	−8.3	68.90	10.2
18	7845	Drab silty clay, pebbles and lime	18.0	27.2	−9.2	84.64	10.5
		Brown gray silt loam:					
19	7801	Brown gray silt loam on tight clay	61.5	68.7	−7.2	51.84	9.3
20	7802	Gray silt loam	58.7	58.7	+0.0	.....	8.9
21	7803	Yellow to grayish clayey silt	37.5	37.0	+0.5	0.25	4.7
		Brown sandy loam:					
22	7849	Brown sandy loam	66.3	67.2	−0.9	0.81	9.8
23	7850	Brown sandy loam, some sand	56.8	53.5	+3.3	10.89	10.1
24	7851	Yellow sand, some silt	45.8	42.5	+3.3	10.89	4.2

* In each soil type the first sample represents surface layer of the soil; the second sample in order represents subsurface, and the third one represents subsoil.

TABLE 2—*Continued*

SAMPLE NO.	SOIL SURVEY NUMBERS	SOIL DESCRIPTION BY LAYERS	RECOVERY OF PHOSPHORUS		DEVIATION		ALKALI REQUIRED PER 10 CC. EXTRACTED SOLUTION
			From rock phosphate	From double acid phosphate	+ or −	Squared	
			per cent	*per cent*			*cc.*
		Timber soils					
		Yellow gray silt loam on gravel:					
25	7816	Yellow gray silt loam on gravel	54.7	49.2	+5.5	30.25	12.0
26	7817	Yellow silt loam	46.0	43.0	+3.0	9.00	11.9
27	7818	Yellow clayey silt, some gravel	50.5	45.8	+4.7	22.09	11.8
		Yellow silt loam:					
28	7858	Yellow silt loam, brownish gravelly	70.5	68.5	+2.0	4.00	10.6
29	7859	Yellow silt loam to yellow sandy loam	63.8	66.8	−3.0	9.00	11.4
30	7860	Yellow silt to gravelly sandy silt	62.3	62.0	+0.3	0.09	11.7
		Yellow-gray sandy loam:					
31	7855	Yellow gray sandy loam, some brown	73.0	73.5	−0.5	0.25	12.0
32	7856	Yellow sandy loam, some gray	68.8	73.2	−4.5	20.25	12.1
33	7857	Yellow sand, little silt	68.0	69.5	−1.5	2.25	12.1
		Terrace soils					
		Brown sandy loam:					
34	7852	Brown sandy loam	65.7	64.2	+1.5	2.25	12.0
35	7853	Brown sandy loam, variable	46.5	44.0	+2.5	6.25	12.1
36	7854	Yellow sand, some clayey sand	34.8	34.0	+0.8	0.64	12.0
		River bottom soils					
		Brown mixed loam:					
37	7861	Brown mixed loam	48.5	50.0	−1.5	2.25	9.90
38	7862	Brown mixed loam	42.5	46.3	−3.8	14.44	10.50
39	7863	Yellowish brown loam, some sand	54.8	54.0	+0.9	0.81	11.3
		Deep peat:					
40	7870	Black decomposed peat, shells	102.0	101.0	+1.0	1.00	2.1
41	7871	Black peat	110.8	113.0	−2.2	4.84	7.0
42	7872	Black to brown peat, drab clay at 30 inches	66.8	70.0	−3.2	10.24	8.8
		Algebraic sum of deviations			−15.6	451	
		Mean deviation			−.371		
		Standard deviation $\sqrt{\frac{\Sigma d^2}{N} - m^2} = \sqrt{\frac{451}{42} - .138} = 3.256$					
		Z = ratio of mean deviation to standard deviation $= \frac{-0.371}{3.256} = -0.114$					

tracted from the treated soil. The results represent the net gain due to the treatment; it was assumed that the amount of soil phosphorus extracted from the treated soil is the same under these conditions as the amount of phosphorus extracted from the untreated soil.

An examination of the results in table 2 reveals a rather striking fact, namely, that the degree of recovery of phosphorus from nearly every soil studied is practically the same, regardless of the source of the phosphatic material. Water soluble acid phosphate, after it is incorporated into the soil mass and moistened, becomes soluble in 0.2 *N* nitric acid only to the same extent as the Tennessee rock phosphate. There are some relatively small differences in solubility in some individual cases. On the whole, however, these differences are very unimportant, as one can judge from the application of Student's method of bio-metric analysis (2). Using forty-two soil trials in which the mean deviation is only -0.371, and the standard deviation 3.256, we find that the ratio of the former to the latter, or Z, is only -0.114. This value is too small to be significant, since it is not given in Student's tables for the calculation of probability. The smallest value of Z used in his tables is 1, and such value gives chances from 10 to 12 times as small as those considered at all significant.

Different soil types allow the recovery of different amounts of phosphorus. In this respect, the variations are very great. Thus, the soil of the third layer of the samples of brown silt loam (sample 3, table 2) did not allow any re-recovery; while, in the surface layer of peat, the recovery was complete. Indeed, the amount of phosphorus recovered from peat of the second layer was greater than the amount applied. The differences in phosphorus recovery are from 11 to 13 per cent, and seem to be larger than those which could be ascribed to the experimental error. In the majority of cases, the recovery of phosphorus varied between 40 and 60 per cent. On the whole, the recovery was somewhat greater in the surface layer than in the subsurface. The third layer, or the subsoil, gave the smallest recovery of phosphorus in all cases.

In order to ascertain whether or not other phosphatic fertilizers would follow the same general mode of behavior as observed with the Tennessee rock phosphate and double acid phosphate, the experiment was repeated on another sample of brown silt loam, using various phosphatic fertilizers. As one notices from table 1, these phosphorus-carrying substances varied in their phosphorus content very considerably. The amount of each substance used, however, was in every case equivalent to 4 mgm. phosphorus, as calculated from their analyses. Twenty-five grams of soil was used in every case. The amounts of phosphorus extracted with 0.2 *N* nitric acid, as well as the per cent of phosphorus recovery are given in table 3. The results show that, with the exception of iron phosphate and two or three brands of slag, the per cent of recovery is practically the same for the various phosphatic carriers. Acid phosphate gave no larger recovery than the majority of the so-called insoluble phosphatic fertilizers. These figures are rather interesting, espe-

TABLE 3

*Recovery of phosphorus from different phosphatic fertilizers applied to brown silt loam**

FERTILIZER	PHOSPHORUS EXTRACTED	PHOSPHORUS EXTRACTED	ALKALI REQUIRED PER 10 CC. OF EXTRACTED SOLUTION
	mgm.	*per cent*	*cc.*
Tennessee rock phosphate	2.35	58.8	11.6
Slag A	2.12	53.0	11.4
Slag B	2.11	52.8	11.4
Slag C	2.16	54.0	11.4
Slag D	2.33	58.3	11.4
Birmingham slag	2.23	55.8	11.5
Blue rock	2.28	57.0	11.6
Florida soft rock	2.37	59.3	11.6
Apatite	2.40	60.0	11.6
Iron phosphate	1.91	47.8	11.7
Aluminum phosphate	2.32	58.0	11.6
Acid phosphate	2.29	57.3	11.6
Steamed bone meal	2.15	53.8	11.6
Soil, alone			11.7
Acid, alone			12.7†

* In each case 4 mgm. of phosphorus were applied per 25 gm. of soil.

† 10 cc. of distilled water was used to wet the soil after fertilizer was added to it. In order to make the results comparable, 10 cc. of water was added to 250 cc. of acid before titration.

TABLE 4

*Phosphorus extracted with distilled water and with 0.2 N nitric acid from different phosphatic fertilizers**

FERTILIZER	WATER SOLUBLE PHOSPHORUS EXTRACTED		PHOSPHORUS SOLUBLE IN 0.2N HNO_3 AND EXTRACTED		ALKALI REQUIRED PER 10 CC. EXTRACTED SOLUTION
	mgm.	*per cent*	*mgm.*	*per cent*	*cc.*
Tennessee rock phosphate	0.08	2.0	3.94	98.6	13.0
Double acid phosphate	3.60	90.0	4.19	105.0	13.0
Slag A	0.00	0.0	3.89	97.3	12.9
Slag B	0.03	0.8	3.98	99.5	12.9
Slag C	0.23	5.8	4.05	101.0	12.8
Slag D	0.06	1.5	4.02	100.5	12.8
Birmingham slag	0.09	2.3	3.96	99.0	12.9
Blue rock	0.16	4.0	4.02	100.0	13.1
Florida soft rock	0.09	2.3	3.98	99.5	13.0
Apatite	0.01	0.3	4.08	102.0	13.0
Iron phosphate	0.15	3.8	3.72	93.0	13.1
Aluminum phosphate	0.22	5.5	4.07	101.8	13.1
Acid phosphate	3.40	85.0	3.88	97.0	13.1
Steamed bone meal	0.20	5.0	4.01	100.2	13.0
Acid alone					13.1

* Two hundred and fifty cubic centimeters of either acid or water were used on fertilizer which contained 4 mgm. of phosphorus per sample.

cially if one considers them in parallel with the data presented in table 4 which gives the amount and the per cent of phosphorus recovery from the same amount of fertilizing material alone (without the soil), when the extraction was made either with distilled water, or with fifth normal nitric acid.

The data in table 4 show that the phosphorus in acid phosphate is recovered with distilled water to the extent of 85 per cent, and from double acid phosphate to the extent of 90 per cent. None of the other phosphates had a solubility in water amounting to six per cent, and some of them, as apatite and one of the slags, were extremely insoluble in water.

When the same materials were extracted with 0.2 *N* nitric acid, under the same conditions, i.e., without mixing them with the soil, the per cent of recovery was about 100 in nearly every case (See table 4).

It is evident that there is something in the soil that prevented this phosphorus recovery. Undoubtedly some of the acid, after it is added to the soil, reacts with some of the soil bases, forming nitrates. This would be especially true if carbonates of calcium and magnesium are present. Such a reaction would decrease the concentration of the acid, and thus cause the decrease in the amount of phosphorus extracted. Anticipating such action in some soils that are more or less supplied with carbonates, an aliquot of clear extracted solution was taken and titrated against a standard alkali (0.1484 normal), using methyl-red-para-nitro-phenol for the indicator. The figures for relative titrations are given in tables 2, 3 and 4 (last column). They show that fertilizing materials alone do not reduce the concentration of nitric acid to any appreciable extent (table 4). The fertilizing materials after they are applied to brown silt loam, as recorded in table 3, reduce the acid concentration rather uniformly to about 90 per cent of its original strength. This in no way accounts for the reduction of phosphorus recovery to about 50 or 60 per cent of its recovery from the fertilizing materials themselves. The titrations recorded in table 2 explain the failure of phosphorus recovery in only a very limited number of cases. Sample 3, or the subsoil layer of brown silt loam, contained a large amount of carbonates, which used practically all the acid present, thus making the phosphorus extraction impossible. Perhaps samples 21 and 24 also behaved in a similar way. With these three exceptions, however, the reduction in the acid concentration fails entirely to explain the behavior of phosphorus in all these soils. The lack of correlation between acid concentration and the ultimate phosphorus recovery is very apparent, if one compares the surface soil with its subsurface and subsoil layers in regard to the phosphorus extraction and the concentration of nitric acid at the end of the extraction. Peat, represented by samples 40, 41, and 42, affords an interesting observation. The carbonates of the surface layer reduce the acid concentration to about one-sixth of its original strength. In spite of that, the phosphorus recovery was practically complete. In the subsoil layer, sample 42, the acid concentration was over four times as great as in the surface layer, yet the phosphorus recovery was reduced to 70 per

cent. Again, with the acid in the subsurface layer, sample 41, slightly weaker than that in the subsoil layer, the recovery was complete. There was even some stimulating effect noticed on the soil phosphorus.

Very little or no correlation can be traced if one compares, in this respect, the surface, subsurface or the subsoil layers among themselves. Noticing the fact that the subsoil layer of the peat soil contains a considerable amount of clay particles or mineral matter, the suggestion arises that the mineral portion of the soil forces phosphorus to react in the way here observed. It would seem probable that some double salts of phosphorus with iron or aluminum, or with both, are formed that are less soluble than the simple phosphates of calcium, iron and aluminum. The presence of silica in the form of silicic acid perhaps has considerable influence on the formation of these complex combinations. However, the presence of bases commonly found in the soil is evidently essential for their formation. The silica of quartz sand, which was rather coarse in texture, prevented some phosphorus recovery, as may be noted in figure 3. In this figure, data of another experiment are shown where different amounts of phosphorus were added to 25 gm. of quartz sand, and later extracted with 0.2 *N* nitric acid.

TABLE 5

*Recovery of phosphorus from 25 gm. of brown silt loam and yellow-gray silt loam**

	PHOSPHORUS EXTRACTED							
	First		Second	Third	Fourth	Fifth	Total	
	mgm.	*per cent*	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*per cent*
Brown silt loam:								
With rock phosphate.....	1.86	46.5	0.47	0.24	0.13	0.09	2.79	69.8
With double acid phosphate..	1.75	43.8	0.46	0.21	0.12	0.02	2.56	64.0
Yellow-gray silt loam:								
With rock phosphate.....	3.02	75.5	0.25	0.09	0.02	0	3.38	84.5
With double acid phosphate..	3.10	77.5	0.24	0.10	0.05	0.01	3.50	87.5

* Treated with 4 mgm. of phosphorus of either Tennessee rock phosphate or double acid phosphate. Five consecutive extractions were made with fifth normal nitric acid.

At this point, it is desirable to emphasize the fact that the phosphorus, which 0.2 *N* nitric acid fails to extract from a given soil, exists in the soil in such a complex combination that even subsequent extractions with fresh nitric acid of the same strength fail to bring the phosphorus into solution. Separate portions of two soils, brown silt loam and yellow gray silt loam, were treated with Tennessee rock phosphate and double acid phosphate. The extractions with nitric acid were filtered and the residues washed four times with warm distilled water. The residue was treated with fresh nitric acid, and the procedure was repeated five times. The results are presented in table 5, and show that but a relatively small amount of phosphorus was extracted from those soils after the first extraction, and the amount decreased with every subsequent extraction.

FACTORS MODIFYING THE PHOSPHORUS RECOVERY FROM SOILS

The factors that may modify the behavior of phosphorus in soil are (a) time of reaction, (b) temperature during the reaction, (c) moisture content of soil, (d) amount of fertilizer applied, and (e) chemical nature of various substances that are used in agricultural practice or are present in soils in different amounts.

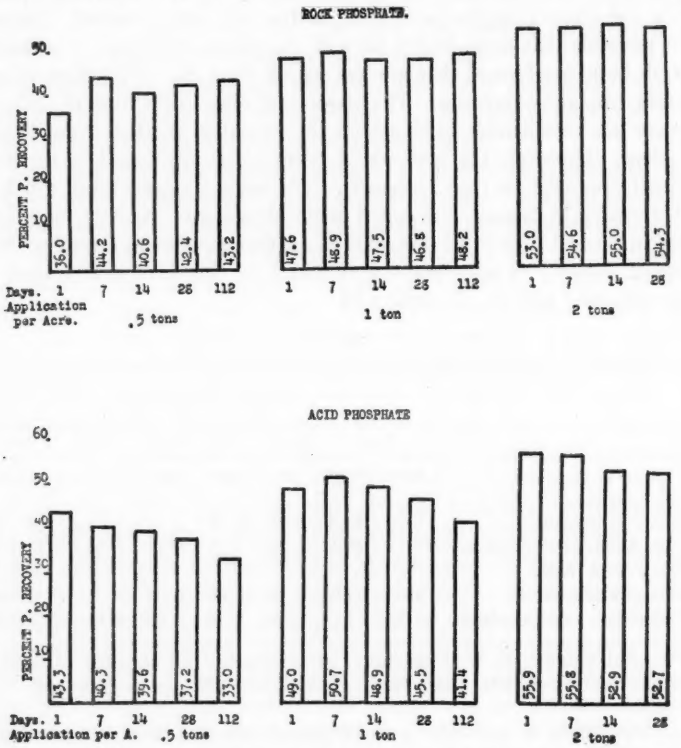

FIG. 1. EFFECT OF TIME OF REACTION AND THE AMOUNT OF PHOSPHORUS PRESENT ON THE PER CENT OF PHOSPHORUS RECOVERY FROM BROWN SILT LOAM

The phosphorus was added to the soil in the form of either rock or acid phosphate; 0.2 *N* HNO_3 was used for extraction.

Time of Reaction

In most of the chemical reactions, time is a very important factor. In order to determine the extent of its importance in reactions between soluble acid phosphate and the soil bases, the influence of time was studied with two soils and with quartz sand. The experiments were arranged in such a way that the influence of amounts of fertilizers present for reaction was also studied

at the same time. Twenty-five gram portions of soil were treated with 0.0125 gm., 0.025 gm. and 0.0500 gm. of Tennessee rock phosphate and double acid phosphate, the amounts being equivalent to 1000, 2000 and 4000 pounds of fertilizer per acre (2,000,000 pounds of soil), respectively. Complete sets of the treated soils, moistened with distilled water, were left for various lengths of time, after which the extractions with 0.2 *N* nitric acid were made and the phosphorus determined.

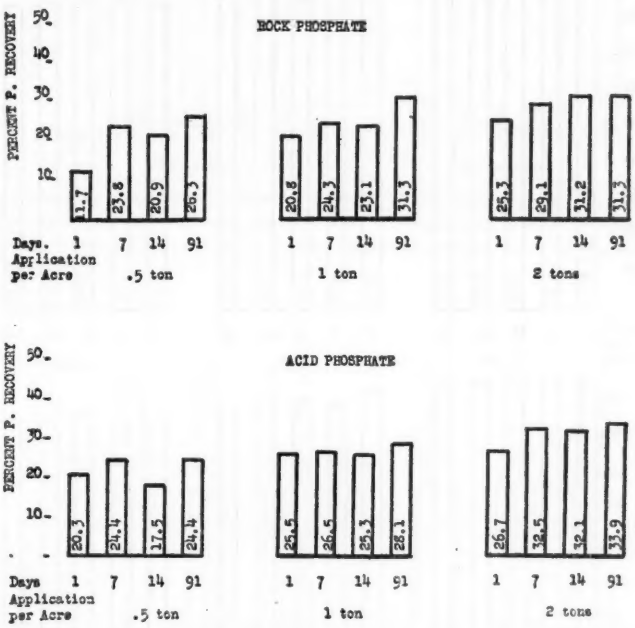

FIG. 2. EFFECT OF TIME OF REACTION AND THE AMOUNT OF PHOSPHORUS PRESENT ON THE PER CENT OF PHOSPHORUS RECOVERY FROM BLACK CLAY LOAM

The phosphorus was added in the form of either rock or acid phosphate; 0.2 *N* HNO_3 was used for extraction.

The results are presented in figures 1, 2 and 3, and they show that, in a general way, the reaction is complete in one day. In brown silt loam, treated with double acid phosphate, the phosphorus recovery is slightly, but consistently, decreased with the increase in the time allowed for the reactions. This tendency was not observed in black clay loam or in quartz sand. The greatest recovery in every case was obtained in quartz sand, and the smallest in black clay loam, the brown silt loam occupying the intermediate position.

Moisture content

In all the experiments recorded here, optimum moisture content (between 50 and 70 per cent of saturation) was maintained in soils treated with phosphatic fertilizers. This factor, as one notices in figure 4, is not as essential

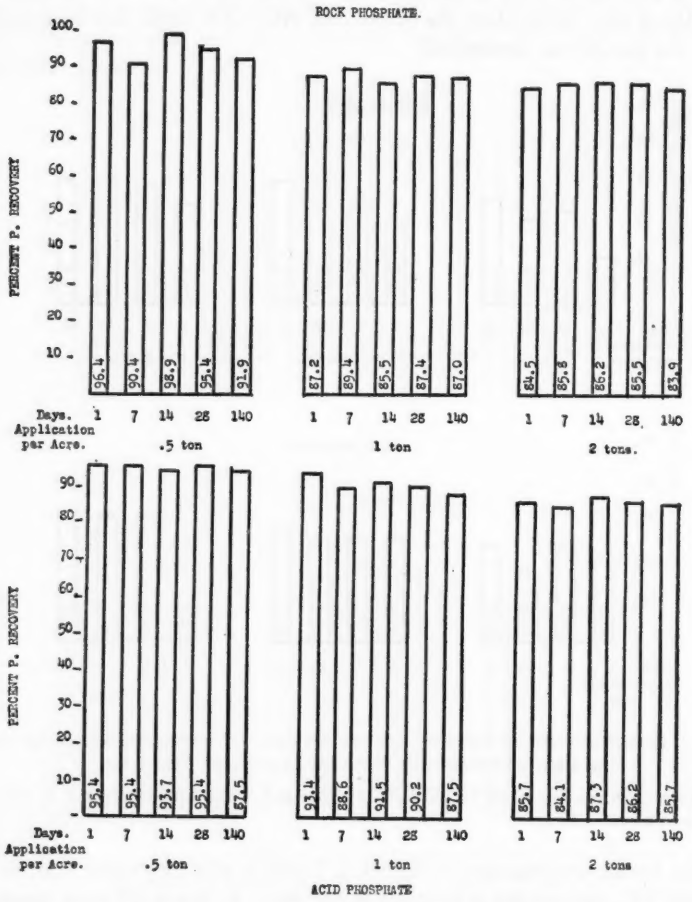

FIG. 3. EFFECT OF TIME OF REACTION AND THE AMOUNT OF PHOSPHORUS PRESENT ON PER CENT OF PHOSPHORUS RECOVERY FROM QUARTZ SAND

The phosphorus was added in the form of either rock or double acid phosphate; 0.2 *N* HNO_3 was used for extraction.

as might be expected. The reaction appears to take place after nitric acid is applied for the extraction, proceeds in rather strongly acid solutions, and is completed during the three hours of shaking in the shaking machine.

In several lots of brown silt loam, increasing moisture contents were maintained at from 10 to 100 per cent of saturation. The phosphorus recovery was practically the same in all trials with rock phosphate, and within 6 per cent in the case of double acid phosphate.

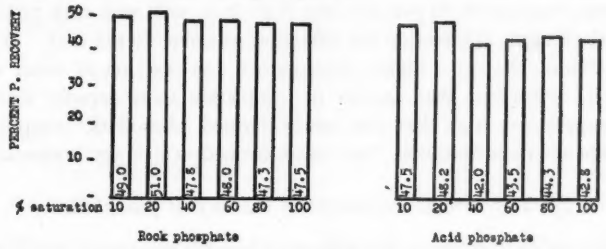

FIG. 4. EFFECT OF MOISTURE CONTENT IN BROWN SILT LOAM ON THE PER CENT OF PHOSPHORUS RECOVERY FROM 25 MGM. OF THIS SOIL, TREATED WITH 4 MGM. OF PHOSPHORUS IN EITHER ROCK PHOSPHATE OR IN DOUBLE ACID PHOSPHATE; 0.2 *N* HNO_3 WAS USED FOR EXTRACTION

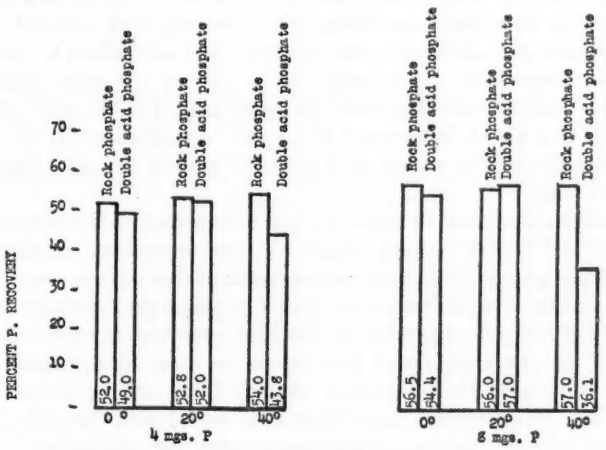

FIG. 5. EFFECT OF TEMPERATURE ON THE AMOUNT OF PHOSPHORUS EXTRACTED FROM 25 GM. OF BROWN SILT LOAM, TREATED WITH 4 OR 8 MGM. OF PHOSPHORUS IN THE FORM OF EITHER ROCK OR ACID PHOSPHATE

The degrees indicate the temperature at which soils, treated with phosphatic fertilizers, were kept for 7 days before extraction. Data represent per cent of phosphorus recovery with 0.2 *N* HNO_3.

Temperature

The temperature at which reaction takes place was studied with brown silt loam soil, which was kept at 0°, 20°, and 40°C. As one notices in figure 5, at all three temperatures, the recovery of phosphorus from rock-phosphate-treated soil was practically the same. This holds true whether 4 or 8 mgm.

of phosphorus were originally applied. Double acid phosphate offers the same recovery of phosphorus at two of the temperatures studied; namely, at 0° and 20°C. At 40°C., however, the phosphorus recovery does not follow the general tendency. In the application amounting to 4 mgm. of phosphorus the recovery was about 10 per cent less than from soils with rock phosphate, while in the 8 mgm. application the difference was over 20 per cent. It would seem, therefore, that at a higher temperature, the reaction of water soluble double acid phosphate was carried to completion more rapidly than at a lower temperature, and that the newly formed phosphatic compound or compounds are more insoluble than those formed at a lower temperature.

Effect of various substances on recovery of phosphorus

It is reasonable to suppose that different chemical substances would modify the mode of reaction of soluble phosphatic compounds with soil, as well as to modify the character of the resultant soil solution. Two different soils, brown silt loam and yellow gray silt loam, a prairie and a timber soil, respectively, were treated with various substances which are often used in farm practice. The soils later were treated with Tennessee rock and with double acid phosphate and phosphorus was extracted and determined in the usual way. For comparison, quartz sand was treated in the same way. The substances used in this experiment included CaO, $CaCO_3$, KCl, $NaNO_3$, $(NH_4)_2SO_4$, and $CaSO_4$ in amounts of 0.1 gm. of substances per 25 gm. of yellow gray silt loam or quartz sand, and 0.05 gm. for the same amount of brown silt loam.

The results summarized in tables 6, 7 and 8 show that, in the amounts here used, KCl and $NaNO_3$ did not influence to any appreciable extent the recovery of phosphorus either from rock or double acid phosphate treated soils. CaO and $CaCO_3$ were also without any effect on yellow gray silt loam or sand, while they caused some depression in phosphorus recovery in brown silt loam.

Both of the above mentioned sulfates, on the other hand, caused a considerable increase in the phosphorus recovery from both agricultural soils. The recovery was somewhat larger from soils treated with the easily soluble phosphatic fertilizer than from those treated with rock phosphate.

In the case of quartz sand, treated with rock phosphate, the recovery was not affected, while a little increase was observed in sand treated with double acid phosphate. The increase in the latter case could hardly be called significant, while the increase in phosphorus recovery from the agricultural soils is too great to be attributed to experimental error.

If these results are reliable, they may throw some light on the question of the effect of application of gypsum to soils. The low phosphorus content is a limiting factor in a great many agricultural soils. The application of gypsum to some of these soils causes an increase in crop production. It would seem that, by modifying the character of the soil solution, gypsum indirectly causes a greater availability of phosphorus to plants. This would

TABLE 6

*Effect of various substances on the amount of phosphorus extracted with 0.2 N HNO_3 from brown silt loam**

		PHOSPHORUS EXTRACTED	
		After subtracting blank	Increase over soil treated with phosphorus only
		mgm.	*per cent*
Rock phosphate alone		1.85	
Rock phosphate	+CaO	1.72	−7.0
	+$CaCO_3$	1.73	−6.5
	+KCl	1.84	−0.5
	+$NaNO_3$	1.84	−0.5
	+ $(NH_4)_2SO_4$	2.12	14.6
	+$CaSO_4$	2.16	16.8
Acid phosphate alone		1.59	
Acid phosphate	+CaO	1.57	−1.3
	+$CaCO_3$	1.63	2.5
	+KCl	1.67	5.0
	+$NaNO_3$	1.66	3.8
	+$(NH_4)_2SO_4$	2.03	27.7
	+$CaSO_4$	2.01	26.4

* Treated with either rock or acid phosphate that contained 4 mgm. of phosphorus. Amount of CaO or salt used = 0.05 gm. per 25 gm. of soil.

TABLE 7

*Effect of various substances on the amount of phosphorus extracted with 0.2 N HNO_3 from 25 gm. of yellow-gray silt loam**

		PHOSPHORUS RECOVERY	
		After subtracting blank	Increase over soil treated with phosphorus only
		mgm.	*per cent*
Rock phosphate alone		2.79	
Rock phosphate	+CaO	2.77	0
	+$CaCO_3$	2.74	−2
	+KCl	2.79	0
	+$NaNO_3$	2.77	0
	+$(NH_4)_2SO_4$	3.31	19
	+$CaSO_4$	3.28	18
Acid phosphate alone		2.78	
Acid phosphate	+CaO	2.87	3
	+$CaCO_3$	2.83	2
	+KCl	2.89	4
	+$NaNO_3$	2.81	1
	+$(NH_4)_2SO_4$	3.48	25
	+$CaSO_4$	3.46	24

* Treated with 4 mgm. phosphorus in the form of either rock or acid phosphate. Amount of CaO or salt used = 0.1 gm.

TABLE 8

*Effect of various substances on the amount of phosphorus extracted with 0.2 N HNO_3 from 25 gm. quartz sand**

		PHOSPHORUS RECOVERY	
		After subtracting blank	Increase over soil treated with phosphorus only
		mgm.	*per cent*
Rock phosphate alone		3.44	
Rock phosphate	CaO	3.45	0
	+$CaCO_3$	3.42	−1
	+KCl	3.37	−2
	+$NaNO_3$	3.29	−4
	+$(NH_4)_2SO_4$	3.43	−1
	+$CaSO_4$	3.52	2
Acid phosphate alone		3.43	
Acid phosphate	+CaO	3.53	2
	+$CaCO_3$	3.42	−2
	+KCl	3.42	−2
	+$NaNO_3$	3.52	1
	+$(NH_4)_2SO_4$	3.72	7
	+$CaSO_4$	3.69	6

* Treated with either rock or acid phosphate that contained 4 mgm. phosphorus. Amount of CaO or salt used = 0.1 gm.

TABLE 9

*Effect of calcium carbonate upon recovery of phosphorus from 25 gm. brown silt loam**

	PHOSPHORUS IN EXTRACT	PHOSPHORUS IN EXTRACT DUE TO TREATMENT	PHOSPHORUS RECOVERY
	mgm.	*mgm.*	*per cent*
Soil alone	0.31		
Soil + rock phosphate	2.01	1.70	42.5
Soil + rock phosphate + 1 gm. $CaCO_3$	1.04	0.73	18.3
Soil + rock phosphate + 2 gm. $CaCO_3$	0.12	−0.19	−4.8
Soil + rock phosphate + 4 gm. $CaCO_3$	0.00	−0.31	−7.8
Soil + double acid phosphate	1.94	1.63	40.8
Soil + double acid phosphate + 1 gm. $CaCO_3$	0.99	0.68	17.0
Soil + double acid phosphate + 2 gm. $CaCO_3$	0.12	−0.19	−4.8
Soil + double acid phosphate + 4 gm. $CaCO_3$	0.06	−0.25	−6.3

* Treated with 4 mgm. of phosphorus of either Tennessee rock phosphate or double acid phosphate. 0.2 *N* HNO_3 was used for extraction.

explain in part the beneficial effect of gypsum on soils depleted in productivity. Evidently, a similar line of reasoning could be applied to ammonium sulfate, though this salt also supplies nitrogen, the soil content of which may also be a limiting factor in crop production.

It was noticed that lime and calcium carbonate, when used in small amounts, do not cause any decrease in the phosphorus recovery. It is sometimes observed in plot work or actual field practice that excessive amounts of limestone in soil inhibit the use of phosphorus by crops. To study this question in the light of the method of testing used in the present study, brown silt loam was treated with 1, 2, and 4 gm. of $CaCO_3$ per 25 gm. of soil. Afterwards this soil was treated with 4 mgm. of phosphorus in the form of either rock or double acid phosphate, moistened, allowed to stand, and then phosphorus was extracted as usual. Table 9 shows the results of this experiment. The phosphorus recovery in Brown silt loam, treated with the two phosphatic fertilizers, is practically the same, the figures being 40.8 and 42.5 per cent. One gram of $CaCO_3$ per 25 gm. of soil reduces this recovery to only 17 and 18.3 per cent. Two grams of $CaCO_3$ does not allow any recovery of phosphorus. Indeed, the total amount of phosphorus extracted is less than from the soil not treated with the phosphatic fertilizer. Evidently, even the extraction of soil phosphorus is inhibited. In the case of soil treated with 4 mgm. of $CaCO_3$ this inhibitive effect is still more pronounced. In one case only a trace of phosphorus was found.

The results obtained in this experiment could be anticipated on the ground that most, if not all, of the acid was neutralized by limestone, thus causing the phosphorus extraction to be effected by a neutral salt solution, whose power for solution of phosphatic compounds is naturally very low. The observed phenomenon is somewhat comparable to that observed in actual farm practice. Limestone present in soil in excessive amounts may neutralize the acid soils so completely and so quickly after they have been formed that phosphorus in the resultant neutral or even alkaline medium could not go into solution fast enough for the need of rapidly growing crops.

CONCLUSIONS

The results of these experiments seem to justify the following general conclusions:

1. After phosphorus in the form of phosphatic fertilizers is applied to ordinary mineral soils, it becomes considerably less soluble in 0.2 *N* nitric acid.

2. Peat soil is an exception in that it does not depress the recovery of phosphorus under the same conditions.

3. After phosphatic fertilizers are applied to the soil, the recovery of phosphorus from soil treated with double acid phosphate is no greater than the recovery of phosphorus from the same soil treated with ground rock phosphate, using 0.2 *N* nitric acid for the solvent in each case.

4. After the first extraction with 0.2 *N* nitric acid, the subsequent extractions with fresh acid fail to extract a considerable amount of additional phosphorus. Five consecutive extractions fail to recover the entire amount of phosphorus applied either in the form of rock phosphate or of double acid phosphate.

5. The reaction between the phosphorus of phosphatic fertilizers and the substances present in the soil proceeds very rapidly, the reaction being practically completed in these experiments the first day.

6. The moisture content of soil treated with the phosphatic fertilizer is not a factor in modifying the phosphorus recovery by 0.2 *N* nitric acid extraction.

7. High temperature (40°C. in comparison with 20°C.) may decrease the availability of phosphorus in acid phosphate treated soil, while it has no influence on rock phosphate. Phosphorus recovery is practically the same at temperatures of 0° and 20°C.

8. Of the various supplementary substances used (0.05 −0.10 gm. per 25 gm. of soil), CaO, $CaCO_3$, KCl and $NaNO_3$ do not materially affect the phosphorus recovery from rock or acid phosphate treated soils. This is in direct contrast with $(NH_4)_2SO_4$ and $CaSO_4$ which increase the phosphorus recovery very considerably, $(NH_4)_2SO_4$ causing an increase of 14.6 to 27.7 per cent, and $CaSO_4$ of 16.8 to 26.4 per cent. The latter case may explain in part the beneficial effect of gypsum application to some agricultural soils.

9. Calcium carbonate, in large amounts, inhibits phosphorus recovery, the effect being very much in proportion to the amount of limestone present in the soil. This finding is in agreement with observations that are sometimes made in farm practice.

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OXIDATION OF AMMONIA AND NITRITES BY MICROÖRGANISMS UNDER DIFFERENT CONDITIONS[1]

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Investigators have long realized that for vigorous nitrification both in the field and in the laboratory proper conditions of aeration and reaction of medium must be present.

As early as 1877 (12) when the study of nitrification was still in its pioneer stage, Schloesing and Müntz observed that for strong nitrate production an abundant supply of air is necessary. They wrote two years later (13) that the access to oxygen is an essential condition for vigorous nitrification. Schloesing (11) determined the amount of oxygen necessary to oxidize ammonia to nitrate and found a definite ratio. Winogradsky (14) writing on the oxidation of NH_3 in pure cultures makes the statement that the favorable influence of a more perfect aeration (in liquid cultures) is very marked. In 1903 Boullanger and Massol (4) incubated their cultures in Erlenmeyer flasks containing slag (scories cassés en petite morceaux) broken into small pieces, thus increasing the surface of their liquid cultures. They shook the flasks three or four times every day. Rapid nitrification was observed. Müntz and Laine (10) worked out an arrangement based on the same principle as above with the exception that they used bone black and peat instead of "scories." of Boullanger and Massol with the result that they obtained intensified nitrification. Barthel (1) claimed that by his aeration method a strong nitrification took place. The use of large bottomed shallow vessels has found favor with many investigators. Löhnis and Green (6) obtained maximum oxidation when the ratio between the depth and surface of the layer of culture medium was 1 to 90. Meyerhof (9) very considerably accelerated nitrification by the simple means of passing air through his culture media. Bonazzi (2) obtained greater intensity in nitrification by exposing larger surface and by constantly changing the surface exposed to air. He does not, however, think that increased availability of air to the culture had anything to do with the increase in nitrification. Boullanger (3) followed the work he had done with Massol in 1903. This time he used peat and carried out the experiment on a larger scale to see if production of nitrates by biological process could be put on a commercial basis. He let a solution of $(NH_4)_2SO_4$ flow through several cubic meters of peat inoculated with the nitrifying organisms. The amount of liquid passed through the peat daily was 200 liters containing 7.5 gm. $(NH_4)_2SO_4$ per liter. He obtained in the solution at the exhaust 138.2 gm. of calcium nitrate per liter.

EXPERIMENTAL

In the preliminary work of isolation of the nitrifying organisms which has been described elsewhere it was found that the oxidation of $(NH_4)_2SO_4$ in 25

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[2] The author is indebted to Dr. P. E. Brown, Dr. Paul Emerson and Dr. R. E. Buchanan for advice in this work.

cc. of nutrient solution containing 0.1 per cent of this salt took at the least 9 to 10 days even though 1 cc. of inoculum was used. To increase the rate of oxidation the following experiment was carried out.

Oxidation of Sodium Nitrite

One-pint milk bottles were fitted with double-holed rubber stoppers through which were passed glass tubes bent at right angles, one of them reaching the bottom of the bottles. They were sterilized and into each was put 200 cc. of a sterile solution which contains:

$NaNO_2$	1.0 gm.
Na_2CO_3	1.0 gm.
K_2HPO_4	0.5 gm.
NaCl	0.5 gm.
$MgSO_4$	0.3 gm.
$Fe_2(SO_4)_3$	trace
Water (conductivity)	1000 cc.

These solutions were inoculated with a culture of nitrate former which had gone through a number of subcultures. Sterile moist air was drawn through the solution. The determination of nitrates was made by the phenol-disulfonic acid method and the hydrogen-ion concentration by the "color standards" of Medalia (7); advance information of the material published later by Medalia (8) was also used.

As will be seen from table 1 it took one week by this method of aeration for the complete oxidation of the nitrite solution, whereas without aeration it usually took more than one week to oxidize 25 cc. of the same medium. The rate of oxidation with aeration was 28.6 mgm. $NaNO_2$ per day. The experiment was repeated with the results recorded ("second test"). Oxidation during the period of the experiment took place at the maximum rate of 31.4 mgm. of $NaNO_2$ per day.

Oxidation of $(NH_4)_2SO_4$

The apparatus used for the oxidation of $(NH_4)_2SO_4$ was the same as that used for the oxidation of $NaNO_2$. A solution containing the following nutrients was used:

$(NH_4)_2SO_4$	1.0 gm.
K_2HPO_4	1.0 gm.
NaCl	2.0 gm.
$MgSO_4$	0.5 gm.
$Fe_2(SO_4)_3$	trace
Water (conductivity)	1000 cc.

Two hundred cubic centimeters of the sterile solution was placed in sterile pint bottles and inoculated with a liquid culture of nitrite former. Moist

sterile air was drawn through the solution. The nitrites were determined by the colorimetric method using sulfanilic acid and alpha-naphthylamin hydrochloride in acetic acid.

The results reported in table 2 were at first difficult to understand. The activity of the organism as indicated by the production of NO_2 was very slow.

TABLE 1

The oxidation of sodium nitrite

DATE	$NaNO_2$* OXIDIZED TO NITRATE IN TRIPLICATE SAMPLES			REACTION		
	1	2	3	1	2	3
	mgm.	*mgm.*	*mgm.*	*pH*	*pH*	*pH*
			First test			
April 26	0	0	0	8.5	8.5	8.5
April 28	52.4	65.5	78.5	8.4	8.4	8.4
May 1	186.1	177.1	128.5	8.5	8.6	8.6
May 3	200.0	200.0	200.0	8.6	8.6	8.6
			Second test			
May 6	0	0	0	...	...	...
May 7	20.3	20.3	20.3	8.8	8.8	8.8
May 9	32.7	33.9	55.2	8.8	8.8	8.8
May 11	157.1	151.8	151.8	8.6	8.6	8.6

*Total $NaNO_2$ present 200 mgm.

TABLE 2

The oxidation of $(NH_4)_2SO_4$

DATE	$(NH_4)_2SO_4$* OXIDIZED TO NITRITE IN TRIPLICATE SAMPLES			REACTION		
	1	2	3	1	2	3
	mgm.	*mgm.*	*mgm.*	*pH*	*pH*	*pH*
April 26	0	0	0	7.1	7.1	7.1
April 28	0	8.98	2.8	7.1	7.0	7.0
May 1	2.6	21.3	Trace	7.1	6.6	6.6
May 3	8.4	22.0	Trace	6.9	6.4	6.9
May 5	17.2	24.3	Trace	6.8	6.4	6.8
May 6	29.4	26.0	Trace	6.6	6.3	6.9
May 7	31.8	26.0	2.3	6.5	6.4	6.9
May 9	36.0	26.0	4.3	6.2	6.4	6.5
May 15	44.1	....	...	6.2	...	...

*Total $(NH_4)_2SO_4$ present 200 mgm.

For the first five days only a trace of nitrite was observed. Then the amount of nitrite increased more rapidly in two of the cultures, while culture no. 3 did not show much activity until the end.

The explanation was to be found in the reaction of the medium which was determined every time the solution was tested for nitrite. The solution was

about neutral at the start and as the activity of the organism increased the acidity of the solution increased. Since there was no base supplied the acid could not be neutralized.

The results indicated that even the neutral solution does not support much activity and whatever oxidation occurred was very slow.

In the following experiment with ammonia oxidation, the solution was supplied with an excess of $MgCO_3$ to react with the acid produced.

As will be seen from table 3 culture no. 1 oxidized all of the ammonium sulfate in 11 days. Its rate of oxidation was about 18 mgm. per day. In cultures 5 and 6 mono-and di-basic phosphates respectively were used. Evidently there was not much difference between the two forms of phosphorus.

TABLE 3

The oxidation of $(NH_4)_2SO_4$ in the presence of $MgCO_3$

CULTURE NUMBER	DATE	$(NH_4)_2SO_4$ OXIDIZED TO NITRITE	REACTION
		mgm.	*pH*
1	May 28	0	8.1
1	June 9	200.0	8.1
5 (KH_2PO_4)	June 7	0	8.1
5	June 15	105.0	7.3
6 (K_2HPO_4)	June 7	0	8.1
6	June 15	101.2	7.4

$MgCO_3$ as a base in the oxidation of $(NH_4)_2SO_4$ in solution cultures of nitrite formers was quite without any of the injurious effects as observed by Löhnis and Green (6) or Gaarder and Hagem (5) who tried both $MgCO_3$ and $CaCO_3$ as buffer for their media. The results reported there are in agreement with the recommendation and usage of Winogradsky (14).

Reaction of media

Table 2 clearly indicates that ammonia oxidation takes place very slowly or not at all at pH 7. From the results of table 3 it is plain that at pH 8 intense nitrification takes place. Gaarder and Hagem (5) have shown from their experiments that the optimum for nitrite production is at pH 7.9. Meyerhof (9) on the other hand obtained the maximum nitrite formation at pH 8.4.

Very rapid oxidation of NO_2 takes place according to the results in Table 1 at the reaction of pH 8.5 to 8.8. This result is confirmed by the work of Meyerhof (9) who finds the optimum reaction for the nitrate former between pH 8.3 and 9.3. Gaarder and Hagem (5) obtained maximum oxidation of nitrite at pH 6.8 to 7.3.

To find out if it is possible to further accelerate the rate of oxidation of NH_3 by the nitrifying organisms, the apparatus described below and shown in figure 1 was devised. It was prepared so that it should include the benefit derived from aeration together with the advantage accruing from constantly changing the surface of liquid exposed to the attack of the organisms.

A tube 2.25 inches in diameter and 5 feet 2 inches in length was almost filled with pieces of marble of the size of peas. One end was closed by rubber stopper *S* through which passed tube *A* bent at right angles and projecting about 2 inches into the tube, and a straight glass tube *B* which did not project inside the tube any farther than the rubber stopper. At the other end of the tube a wad of glass wool *W* covering a length of three inches was packed moderately tightly on the column of marble. This end was closed with a rubber stopper through which two glass tubes passed. There was a space of one inch left between the glass wool and the rubber stopper. Tube *E* projected $\frac{3}{4}$ of an inch into this space and directly below it on the glass wool was placed a watch glass *C*.

Another tube 6 feet long and 2.25 inches wide was fitted similarly except that the marble was replaced by clean washed limestone of the size of split peas.

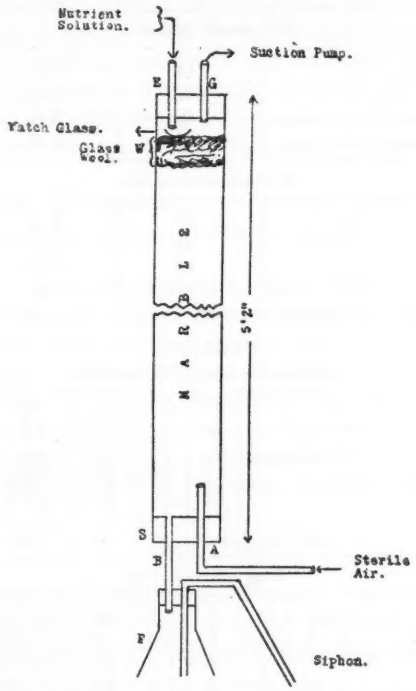

FIG. 1. DIAGRAM OF TUBE ARRANGED FOR OXIDATION OF AMMONIUM SULFATE

Both pieces of apparatus were wrapped in coarse linen and sterilized intermittently with steam. They were set up vertically with the glass wool ends at the top. The straight tube at the lower end was connected to a sterile flask *F* provided with a siphon arrangement. The bent tube was attached to a train of sterile water, sterile cotton and sterile sulfuric acid through which air was drawn. At the upper end tube *E* was connected by a siphon with supply of a sterile ammonium sulfate nutrient solution (no. 1). Tube *G* was connected to the suction pump. To establish a flora of nitrite formers on the marble and on the limestone, 190 cc. portions of two cultures of vigorously oxidizing organisms were allowed to drip slowly through *E*.

A fresh nutrient solution of ammonium sulfate was then allowed to drip slowly through *E* and the suction pump started to draw air through the tubes. The rate of dripping was regulated to four large drops every three minutes. Samples of the solution collected at the bottom in the Erlenmeyer flasks were

TABLE 4

The oxidation of $(NH_4)_2SO_4$ in tubes

DATE AND TIME SAMPLES TAKEN	INTERVAL (RATE OF FLOW WAS 4 DROPS IN 3 MINUTES)	REACTION OF SOLUTION COLLECTED AT BOTTOM	$(NH_4)_2SO_4$ FOUND AS NO_2 PER LITER
	hours	*pH*	*mgm.*
With marble in tube			
July 5	18	6.6	439.0
July 7	48	6.6	613.5
July 9 (11 a.m.)	48	6.6	746.0
July 9 (6 p.m.)	7	7.0	1012.0
With limestone in tube			
July 5	18	6.6	232.4
July 7	48	6.6	381.65
July 9 (11 a.m.)	48	6.6	506.0
July 9 (5 p.m.)	7	7.0	716.0

TABLE 5

Oxidation of $(NH_4)_2SO_4$ in tubes

DATE	PERIOD RUN		RATE OF FLOW PER MINUTE	REACTION IN RECEIVER	AMOUNT OF LIQUID IN RECEIVER	$(NH_4)_2SO_4$ OXIDIZED IN PERIOD RUN	$(NH_4)_2SO_4$ OXIDIZED PER 24 HOURS	EQUIVALENT TO $(NH_4)_2SO_4$ OXIDIZED PER 100 CC.
	hours	*min.*	*drops*	*pH*	*cc.*	*mgm.*	*mgm.*	*mgm.*
With marble in tube								
July 23	5	30	5	6.8	123	19.6	104.6	15.92
July 31	4	0	7	7.3	175	33.78	202.0	19.31
July 31 and August 1	11	0	4.5	7.4	270	75.71	165.4	29.09
August 1	8	0	3	7.3	136	2.04	48.1	3.58
With limestone in tube								
July 23	5	30	5	6.7	230	32.96	175.8	14.3
July 31	4	0	7	7.5	160	22.75	136.5	14.2
July 31 and August 1	11	0	9.5	7.7	480	139.60	304.5	29.0
August 1	8	0	3	7.5	150	106.00	318.0	17.1

taken at different periods and analyzed for nitrite. Table 4 shows the rate of oxidation of ammonium sulfate per liter of solution dripped during different intervals. The maximum rate of oxidation at the given rate of flow was observed in the tube with marble on July 9 between 11 a.m. and 6 p.m. when

266 mgm. of ammonium sulfate per liter were oxidized. This oxidation was caused partly by the organisms in the tubes and partly also by the organisms washed into the flask where the liquid has been accumulating for four days.

To determine the exact amount of ammonium sulfate oxidized per day and to lessen the effect of oxidation in the receiving flash, the outflow liquid was collected and removed for definite intervals, measured, analyzed, and the nitrite content calculated. As seen from table 5 the maximum rate of oxidation in the tube containing marble was 202 mgm. per day. In the tube containing limestone the organism attained a maximum rate of oxidation of 318 mgm. per day. This was assuming that the rate of oxidation throughout the rest of the day remained as high as it was during the eight hours the liquids were collected. This assumption, however, is not warranted because the rate of oxidation is quite irregular. This has been noticed by Bonazzi (2). Winogradsky (14) found that after twenty days, nitrification in one of his cultures remained stationary instead of showing progressive increase as it had done previously.

The washing down of organisms by the dripping liquid might also have had some influence in decreasing the rate of oxidation noticed August 1 in the tube with the marble.

The high rate of oxidation obtained in these experiments is a result of optimum aeration, removal of products of oxidation by the downward flow of liquid and exposing a large surface of liquid to the bacterial activity. Where aeration was practiced as in the case of milk-bottle experiments reported at the beginning less than 20 mgm. of ammonium sulfate was oxidized per day. However, comparisons between these two experiments and especially between those of two different investigators—unless the experiments are conducted on identically similar conditions of apparatus, inoculum, aeration, etc.—are likely to mislead.

CONCLUSIONS

1. When a current of air was passed through a liquid culture of nitrate former in pint milk bottles, 31.4 mgm. of sodium nitrate was oxidized per day

2. Under the same conditions 18 mgm. of ammonium sulfate was oxidized by nitrite formers.

3. When a nutrient solution of ammonium sulfate was allowed to drip into the top of a long tube containing limestone of the size of split peas on the surface of which a flora of nitrite formers had been established and a current of air was drawn through the mass, the rate of oxidation of ammonium sulfate reached the maximum of 318 mgm. per day.

4. Vigorous oxidation of ammonium sulfate by the nitrite formers took place when the reaction of the liquid medium was around pH 8.0. For the nitrate formers the optimum reaction was between pH 8.5 and 8.8.

5. Magnesium carbonate used as a base in the oxidation of ammonium sulfate was without any injurious toxic effect.

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THE EFFECT OF SOIL SUSPENSIONS UPON THE SOLUBILITY OF THE SULFATE RADICAL IN THE SYSTEM $Ca(OH)_2$–$CaSO_4$–H_2O

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INTRODUCTORY

It has been shown (7) that heavy additions of burnt lime have an effect opposite to that of magnesia upon lysimeter leachings of native sulfates from soil, particularly during the first two years (4) after treatment. With increase in lime additions the losses of sulfates derived from soil, rainfall, and treatment-impurities were initially depressed far below the loss from untreated soil. From a related study (6) of sulfur precipitation, it was determined further that the sulfate concentrations of leachings from the heavily limed surface soil were decidedly less than those of the rain waters responsible for leachings. In a later report (8) it was shown that heavy CaO additions were also depressive to outgo of sulfates from three sulfureous treatments, $FeSO_4$, pyrite, and powdered sulfur, each equivalent to 1000 pounds of S per 2,000,000 pounds of soil. The $FeSO_4$ findings militated against the assumption that the depression exerted by CaO upon outgo of sulfates was the result of inhibited sulfofication of native or added sulfur.

But with increase in magnesia additions the sulfate losses were materially increased when no sulfur, save that of rainfall and impurities in treatments, was added to the soil. Magnesia, both light and heavy treatments, also accelerated the outgo of sulfates from additions of $FeSO_4$ and elementary sulfur (8). It was shown further (7) that light applications of both lime and magnesia accelerated the outgo of sulfates derived from native organic forms of sulfur and rainfall and also from ferrous sulfate and elementary sulfur. The reverse was true, however, where pyrite was added. The loss from pyrite alone exceeded that from pyrite supplemented by both light and heavy amounts of CaO and MgO.

In one of the contributions (6) above cited, the data of Cameron and Bell (2) and Seidell (9) were given in parallel with similar data obtained by two analysts in this laboratory to demonstrate that the solubility of $CaSO_4$ was less in the system $Ca(OH)_2$–$CaSO_4$–H_2O than in the system $CaSO_4$–H_2O. Though the influenceof $Ca(OH)_2$ upon the solubility of $CaSO_4$ without contact with soil was positive, it was still insufficient by far to account for the greatly diminished outgo of added sulfates in the lysimeter leachings. The work here reported

was done in an effort to determine the cause for the failure of both added and engendered sulfates to leach from surface soil alone, even after 5 years.

EXPERIMENTAL

As a preliminary step, two points were determined empirically:

A. Absolute occurrences of SO_4 in varying charges of commercial high-calcic lime.

TABLE 1

*Influence of variation in charge upon the hydrochloric acid soluble sulfates in a high-calcic commercial hydrated lime**

CHARGE OF COMMERCIAL SAMPLE	CaO DISSOLVED AS $CaCl_2$	SULFATE FOUND AS $BaSO_4$ EQUIVALENT	
		Per charge	Per 100 gm. of sample.
gm.	*gm.*	*gm.*	*gm.*
1.66	1.137	0.0290	1.75
3.33	2.281	0.0561	1.69
5.00	3.425	0.0860	1.72
6.67	4.568	0.1132	1.70
13.34	9.137	0.2270	1.70
21.20	14.522	0.3590	1.70

* $BaSO_4$ precipitated from a uniform volume of 400 cc.

TABLE 2

*Influence of variation in charge upon the water extractable sulfate in a high-calcic commercial hydrated lime**

CHARGE OF COMMERCIAL SAMPLE PER LITER OF H_2O	$Ca(OH)_2$ PER LITER		WATER SOLUBLE SULFATES AS $BaSO_4$	
	In solution phase	Undissolved excess of solid phase	Per liter of extract	Per 100 gm. of sample
gm.	*gm.*	*gm.*	*gm.*	*gm.*
1.66	1.296	0.118	0.0248	1.499
3.33	1.740	1.106	0.0320	0.961
5.00	1.740	2.520	0.0482	0.964
6.67	1.776	3.894	0.0574	0.860
13.34	1.776	9.590	0.0980	0.720
21.20	1.776	16.286	0.1580	0.745

* $BaSO_4$ precipitated from a uniform volume of 400 cc.

B. Amount of water-soluble $CaSO_4$ recoverable from each of the several charges of the commercial hydrate used alone and with soil in subsequent experiments.

Total SO_4 was determined by making hydrochloric acid solutions of charges ranging between 1.66 gm. and 21.20 gm., barium sulfate precipitations being made from a constant volume of 400 cc. No evidence of H_2S was detected during the boiling of lime with hydrochloric acid.

A. Total SO_4 in $Ca(OH)_2$. The actual charges, CaO as $CaCl_2$ in the HCl solution, $BaSO_4$ determined and $BaSO_4$ per 100 gm. of sample are given in table 1. These results show a constant well within analytical error, and they give no indication of calcium occlusion by the $BaSO_4$ precipitate.

B. Water-soluble SO_4 in $Ca(OH)_2$. Charges 1.5 times those designated in table 1 were then used for 1.5-liter aqueous extractions of sulfate impurities. Titrations were made against 25-cc. aliquots to determine the respective concentrations of $Ca(OH)_2$. Aliquots of 500 cc. were used for duplicate $BaSO_4$ precipitations, the 500-cc. aliquots having been first acidified slightly with HCl and reduced to a constant volume of 400 cc. The $BaSO_4$ occurrence per liter is on the same basis as the total $BaSO_4$ found per corresponding proportionate charges in table 1. The resulting data are given in table 2.

The results of table 2 show a uniform $Ca(OH)_2$ concentration for all charges above the minimum of 1.66 gm. The solid-phase excesses of $Ca(OH)_2$ are given, along with $BaSO_4$ determinations and the calculations on the basis of 100 gm. of charge. The maximum recovery per 100 gm. of lime is less than the maximum in the hydrochloric acid solution. The maximum recovery in each case was obtained from the solution of minimum charge. However, varying from the hydrochloric acid solutions, where the doubling of the charge gave a sulfate recovery slightly less than twofold and probably within analytical error, the doubling of the minimum charge in the aqueous solution caused a very decided drop in the ratio of sulfate recovered to charge used. Further decreases in respective proportions of SO_4 recovered are also shown for increases in bulk of undissolved hydrate. These data demonstrate one point which should interest the commercial chemist and analyst as well as the soil chemist. Water-soluble sulfates can not be determined as a constant in burnt and hydrated high-calcic limes, at least within the time limits designated, since the mass of the solid-phase $Ca(OH)_2$ is a factor as well as saturation of the lime water solution. The measure of sulfates must be the concentration of the unoxidized HCl solution (or equivalent solvent), the calcium concentration of which seems to be of no import within the ranges of 1.66 gm. to 21.20 gm. per liter.

SOLUBILITY OF $CaSO_4$ DERIVED FROM $FeSO_4$ IN $Ca(OH)_2$ SOLUTIONS WITH AND WITHOUT SOIL

We do not know of previous work upon the influence of lime as affecting extractability of soil sulfates. In their studies upon the determination of sulfates in alkali soils, however, Hirst and Greaves (3) state: "In our work on the nitrates . . . . and chlorides . . . . clarifying agents, such as alum and lime, were used with excellent results. For obvious reasons, however, neither of these substances could be used for clarifying solutions in which sulfates are to be determined, particularly if there were any appreciable amounts of sulfate present as is the case with many alkali soils."

In studying the influence of solution and solid-phase excesses of $Ca(OH)_2$ upon the sulfate radical, with and without soil, $FeSO_4$ solutions were used in experiments 1–4, 6, and 7. In agreement with the sulfate additions in the previous lysimeter studies (8) ferrous sulfate additions were made at the rate of 1000 pounds of S per 2,000,000 pounds of soil. The following experiments were carried out, all solutions having been placed in closed containers, unless otherwise stated.

Experiment 1. Immediate addition of lime to aqueous $FeSO_4$-soil suspensions

Each of three charges of $FeSO_4$, equivalent to 0.2500 gm. of sulfur, was dissolved in 3.5 liters of water. To each of these solutions 500 gm. of soil were added and the mixture was thoroughly agitated. Four grams of the commercial hydrate was then added to one solution, 16 gm. to the second, and 50 gm. to the third. The three admixtures were then shaken thoroughly every thirty minutes for seven hours and permitted to stand undisturbed overnight. These three immediate additions of CaO were representative of the 8-, 32-, and 100-ton additions reported upon (7) previously.

A. Aliquots of each supernatant solution were then titrated against phenolphthalein to determine the respective concentrations of $Ca(OH)_2$. Sulfates were also determined upon 500-cc. aliquots, the clear solutions having been first acidified slightly with HCl and concentrated to a volume of 400 cc.

B. The remaining portion of each admixture was again agitated every thirty minutes for a period of seven hours and permitted to stand overnight undisturbed, with repetition of the $Ca(OH)_2$ and sulfate determinations.

C. The residues from *B* were then permitted to stand for 14 days, being agitated once each day, after which the analytical procedure of *A* and *B* was carried out. The sulfate recoveries thus obtained are given in table 3.

The recoveries of *A*, *B*, and *C* are given as grams of $BaSO_4$ per 500 cc. aliquots and as percentages of the respective sulfate totals. Those totals represented the addition-constant plus the determined water-soluble SO_4 variables from the impurities contained in the $Ca(OH)_2$. The 98 per cent recovery of SO_4 from the 8-ton treatment increased to over 100 per cent for both the 48-hour and 16-day intervals. Though the concentration of $Ca(OH)_2$ from the unabsorbed excess of $Ca(OH)_2$ in the 8-ton treatment was only a small fractional part of that from the 32- and 100-ton treatments, and though it decreased decidedly with lengthened period of contact, the causticity and lack of aeration were such as to inhibit biochemical oxidation of the organic sulfur of the soil, and it would therefore seem that the greater recoveries over the longer periods were due to further releases of accumulated soil sulfates. The two heavier additions proved progressively repressive upon sulfate solubility both as to increase in $Ca(OH)_2$ additions and period of contact of soil with $Ca(OH)_2$. With less frequent agitation during the last fourteen days, the three soil suspensions caused definite decreases in the concentrations of the supernatant $Ca(OH)_2$ solutions. The very small recoveries from the two heavier

admixtures of lime with soil were very much less than the water-soluble blanks of table 2, showing that the soil-lime suspensions removed from the solution phase not only the added soluble sulfate, but also most of that carried as impurities in the calcium hydrate—an effect which increased with increase in time of contact.

TABLE 3

Sulfate recovery from aqueous solutions of $FeSO_4$ in soil suspensions, as influenced by immediate additions of $Ca(OH)_2$ (experiment 1)

$Ca(OH)_2$ addition as CaO-equivalent per 2,000,000 lbs. of soil	Titration 0.5 *N* acid per 500 cc. against phenolphthalein after			$BaSO_4$ equivalent in 500 cc.			$BaSO_4$ precipitate from 500 cc. aliquots after addition of lime*					
							After 24 hours A		After 48 hours B		After 16 days C	
	24 hours	48 hours	16 days	Added as $FeSO_4$ in solution	As impurities in charge	Total actually present	Per 500 cc. aliquot	Of total present	Per 500 cc. aliquot	Of total present	Per 500 cc. aliquot	Of total present
tons	*cc.*	*cc.*	*cc.*	*gm.*	*gm.*	*gm.*	*gm.*	*per cent*	*gm.*	*per cent*	*gm.*	*per cent*
8	6.5	3.0	0.9	0.2650	0.0135	0.2785	0.2730	98.0	0.3006	107.9	0.3135	112.2
32	39.5	35.0	28.0	0.2650	0.0540	0.3190	0.0475	14.8	0.0220	6.9	0.0092	2.9
100	44.5	43.5	38.0	0.2650	0.1688	0.4338	0.0470	10.8	0.0137	3.2	0.0070	1.6

* Average of six determinations $FeSO_4$-soil control immediately before addition of lime 0.2207 and 24 hours later without lime 0.2145.

TABLE 4

Sulfate recovery from aqueous solutions of $FeSO_4$ in soil suspensions to which lime was added 24 hours after a 24-hour preliminary contact of $FeSO_4$ solution with soil (experiment 2)*

$Ca(OH)_2$ addition as CaO-equivalent per 2,000,000 lbs. of soil	Titration 0.5 *N* acid per 500 cc. against phenolphthalein after		$BaSO_4$ equivalent in 500 cc.			$BaSO_4$ precipitate from 500 cc. aliquots after addition of lime*			
						After 24 hours		After 15 days	
	24 hours	15 days	Added as $FeSO_4$ in solution	As impurities in charge	Total actually present	Per 500 cc. aliquot	Of total present	Per 500 cc. aliquot	Of total present
tons	*cc.*	*cc.*	*gm.*	*gm.*	*gm.*	*gm.*	*per cent*	*gm.*	*per cent*
8	1.8	1.0	0.2650	0.0135	0.2785	0.2760	99.1	0.3085	110.8
32	38.0	29.0	0.2650	0.0540	0.3190	0.0230	7.2	0.0070	2.2
100	44.5	38.0	0.2650	0.1688	0.4338	0.0155	3.6	0.0052	1.2

* Average of six determinations no-soil control 0.2207 gm. after 24 hours and 0.2145 gm. after 48 hours.

Experiment 2. Twenty-four-hour contact of $FeSO_4$ with soil suspensions before addition of $Ca(OH)_2$

In this experiment the charges and sulfate concentrations were the same as those of experiment 1. In each case the $FeSO_4$ solution was agitated every

half hour with 500 gm. of soil and permitted to stand overnight, after which the lime additions were made and the procedure of experiment 1 was carried out as to titrations and $BaSO_4$ determinations.

The sulfate solutions which were brought into contact with the soil suspensions in the present experiments were well below the saturation of $CaSO_4$. This obtained where the $CaSO_4$ was formed from reaction between $Ca(OH)_2$ and $FeSO_4$, and also where added later as the solid-phase $CaSO_4 \cdot 2H_2O$.

It would be expected that full proportional recovery would have obtained in the 500-cc. aliquots from the soil-$FeSO_4$ controls. The effect of the $FeSO_4$, if not that of $CaSO_4$, also, would be to flocculate the soil suspensions as would an addition of a dilute acid solution upon an acid soil. Brown and Kellog (1) found that a similar condition—sulfate extraction with a dilute HCl solution—resulted in a sulfate recovery below that obtained by water. This was true of both native sulfates and added $MgSO_4$. The failure of the added soluble sulfate of iron to leach from the lysimeters (8), when added alone and with supplements of CaO and MgO after having been subjected to a total rainfall of 256.0 inches over a 5-year period, indicates that the soil-to-water proportions and the agitated suspension conditions imposed by Brown and Kellog, and by us in the present experiments, were more effective than rainfall leachings in removing sulfates from the soil mass. This point will be considered more at length in concluding paragraphs.

The data of table 4 show decreases in $Ca(OH)_2$ concentrations of the supernatant solution similar to those shown in table 3. It also appears that the longer period of contact of $FeSO_4$ solution with soil and delayed addition of CaO gave results corresponding to those obtained with immediate additions of both $FeSO_4$ solution and lime charges to the soil suspensions. This was true for all three rates of lime treatment.

The results of experiments 1 and 2 (tables 3 and 4) show that the soil mass held the added soluble sulfate against the extractions as tenaciously as it did against rainfall leachings in the lysimeters. Those leachings studies (7) showed a parallel between the formation of $CaCO_3$ from added CaO and the release of the sulfate additions to the drainage waters. This transition in the field lysimeters was, however, a matter of months. Experiment 3 was therefore carried out to determine any change in the retentive properties of the soil, as influenced by the immediate reversion of CaO to $CaCO_3$.

Experiment 3. Effect of early conversion of $Ca(OH)_2$ to $CaCO_3$ upon retention of SO_4 by soil suspensions

In this experiment the same charges and concentrations obtained as in experiments 1 and 2. The soil suspensions were twice agitated with the $FeSO_4$ solution during one hour's preliminary contact. The CaO additions were then introduced, the admixtures agitated every half hour for 7 hours, and permitted to stand overnight. Aliquots of 500 cc. in duplicate, were withdrawn and the $Ca(OH)_2$ concentrations and sulfate contents determined.

Solid Na_2CO_3 was then added in slight excess of the amount required to convert all residual $Ca(OH)_2$ to $CaCO_3$. The frequent agitations, overnight standing, and $BaSO_4$ determinations of experiments 1 and 2 were then carried out. The NaOH formed by the reaction of $Ca(OH)_2$ with Na_2CO_3 gave a highly colored supernatant liquid. This contained large quantities of silica, iron, and organic matter, which were filtered with difficulty. One point should be stressed. In soil-lime suspensions the soil colloids were not in evidence; but the hydrated lime represented a mass of material in colloidal and near-colloidal state. On the other hand, after addition of Na_2CO_3 all of the lime was removed from solution as the carbonate, while a large mass of soil materials were dispersed in the colloidal state throughout the liquid medium.

The $BaSO_4$ determinations and percentage recoveries of total sulfates supplied by additions and as treatment-impurities are given in table 5.

TABLE 5

Sulfate recovery from aqueous solutions of $FeSO_4$ plus early additions of excesses of solid phase $Ca(OH)_2$ in soil suspensions before and after conversion of $Ca(OH)_2$ additions into $CaCO_3$ (experiment 3)*

$Ca(OH)_2$ addition as CaO-equivalent per 2,000,000 lbs. of soil	$BaSO_4$ equivalent in 500 cc. aliquots as sums of a constant equivalent addition of 0.2650 gm. plus variable charge impurity	$BaSO_4$ precipitate from 500 cc. aliquots					
		24 hours after addition of $Ca(OH)_2$ to $FeSO_4$ solution in contact with soil		Following addition of slight excess of Na_2CO_3 to $FeSO_4$-$Ca(OH)_2$ soil suspensions			
				After 24 hours		After 15 days	
		Per 500 cc. aliquot	Of that present	Per 500 cc. aliquot	Of that present	Per 500 cc. aliquot	Of that present
tons	*gm.*	*gm.*	*per cent*	*gm.*	*per cent*	*gm.*	*per cent*
8	0.2785	0.2670	95.9	0.3194	114.7	0.3390	121.7
32	0.3190	0.1000	31.3	0.3336	104.6	0.3585	112.4
100	0.4338	0.1010	23.3	0.3670	84.6	0.4393	101.5

* $Ca(OH)_2$ added after 1 hour's contact between $FeSO_4$ solution and soil suspensions.

These data show that the depressive influences of the excess of $Ca(OH)_2$ were in effect upon the added sulfate radical at the end of the preliminary period of 24 hours. As in similar cases in tables 3 and 4, it could not be concluded that the SO_4 decreases are due to the formation of double salts of calcium and iron, for the same result will be shown where the sulfate radical was introduced as $CaSO_4$. But, after a further 24-hour period of contact following the addition of sodium carbonate, the recoveries from the 8-ton and 32-ton treatments were in excess of the respective amounts known to have been introduced as $FeSO_4$ and as treatment impurities. In the case of the 100-ton additions, the recovery was more than three times that obtained after the 24-hour contact of soil and heaviest excess of $Ca(OH)_2$. The agitations during the first twenty-four hours after introduction of Na_2CO_3 were apparently insufficient to bring all of the large excess of $Ca(OH)_2$ into reaction with the Na_2CO_3. Fourteen days later all of the calcium hydrate had apparently been

converted to $CaCO_3$, for the SO_4 recovery then obtained was equal to that supplied both as ferrous sulfate and as lime impurities. Ammonium carbonate produced the same nullifying effect as that produced by the added Na_2CO_3. The resultant solutions were filtered with such difficulty, however, that its use was abandoned.

The recoveries of sulfate after introduction of Na_2CO_3, or $(NH_4)_2CO_3$, might be attributed entirely, or in large part, to the solvent action of the NaOH, or $(NH_4)OH$, engendered through reaction between $Ca(OH)_2$, and Na_2CO_3 or $(NH_4)_2CO_3$, respectively, rather than to conversion of $Ca(OH)_2$ into $CaCO_3$, were it not for the fact that the same result was obtained by aqueous extraction when the excess of $Ca(OH)_2$ was converted to $CaCO_3$ by means of passages of CO_2 into the $Ca(OH)_2$-soil suspensions. After preliminary contact, one of the 32-ton $Ca(OH)_2$-soil admixtures was subjected to a continuous flow of CO_2 with frequent agitations until all hydrate had become carbonated. From the total sulfate addition of 0.3190 gm. $BaSO_4$ equivalent per 500 cc. of 0.2650 gm. derived from the $FeSO_4$ and 0.0540 gm. as impurities in the $Ca(OH)_2$, the recoveries obtained were as follows:

	gm.
After 24 hours contact with $Ca(OH)_2$ and *just before* passage of CO_2.....	0.1000
Immediately after conversion of $Ca(OH)_2$ into $CaCO_3$ by passage of CO_2...	0.3638
Increased recovery due to the carbonate reaction.....	0.2687

The increase of 0.2687 gm. caused by the passage of CO_2 represents full recovery of the addition and demonstrates that most of the absorptive property of this soil for calcium sulfate passes immediately upon the disappearance of $Ca(OH)_2$. It is thus apparent that while in a hydrated condition from an excess of OH-ions supplied by $Ca(OH)_2$, the soil mass possessed marked retentive properties. It is equally apparent that it did not possess those retentive properties when the OH-ions were supplied by NaOH generated by the $Ca(OH)_2$ and Na_2CO_3 reaction.

The sulfate retention in the soil-$Ca(OH)_2$ suspensions could not well be assigned to $Fe_2O_3 \cdot nH_2O$ derived from the ferrous sulfate, because of the small amount so derived, especially since the containers were sealed. This point will be considered further in experiment 7 (table 9).

Experiment 4. Effect of delayed conversion of $Ca(OH)_2$ to $CaCO_3$ upon retention of SO_4 by soil suspensions

This experiment corresponded to experiment 2, where the $FeSO_4$ was in contact with the soil prior to the introduction of $Ca(OH)_2$, which was converted, 24 hours later, to $CaCO_3$ by means of additions of solid-phase Na_2CO_3. Data obtained are given in table 6. These results show an incomplete recovery of the total sulfate additions after the soil alone had been in contact with the $FeSO_4$ solution for the preliminary period of 24 hours prior to the addition of $Ca(OH)_2$. This partial retention of the SO_4 added to the acid soil is in harmony with the previous lysimeter findings (7) relative to the incomplete leaching of

the acid salt from the same acid soil after extended periodic leaching by rain water. The gains in $BaSO_4$ recoveries which followed conversion of the excesses of $Ca(OH)_2$ into $CaCO_3$ show the same order which obtained in experiment 3, where the $Ca(OH)_2$ additions were made almost immediately after the soil charges were suspended in the $FeSO_4$ solutions.

Experiment 5. Influence of $Ca(OH)_2$ solutions upon solubility of freshly precipitated $CaSO_4 \cdot 2H_2O$ with and without soil

In the previous experiments, here reported, the sulfate radical was introduced as $FeSO_4$, in conformity with the sulfate additions to the lysimeters. The reaction between $FeSO_4$ and the excesses of $Ca(OH)_2$ produced $CaSO_4$ in the present experiments and also in the leachings from the lysimeters. In experiment 5, freshly precipitated $CaSO_4 \cdot 2H_2O$ was used as the source of SO_4 in tests

TABLE 6

Sulfate recovery from aqueous solutions of $FeSO_4$ in soil suspensions, the subsequent recoveries after adding excess of $Ca(OH)_2$† and the converting all $Ca(OH)_2$ to $CaCO_3$ (experiment 4)*

As $Ca(OH)_2$ addition CaO-equivalent per 2,000,000 lbs. of soil	$BaSO_4$ equivalent present in 500 cc. aliquot, as sums of a constant $FeSO_4$ solution and impurity variables	$BaSO_4$ precipitate from 500 cc. aliquots					
		From soil suspensions after 24-hour contact of soil and $FeSO_4$ without lime		From soil plus $Ca(OH)_2$ plus Na_2CO_3			
				24 hours after preliminary period of contact of $FeSO_4$ with soil		15 days after preliminary period of contact of $FeSO_4$ with soil suspensions	
		Found	Loss	Found	Gain‡	Found	Gain‡
tons	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*
8	0.2785	0.2350	0.0435	0.3430	0.1080	0.3515	0.1165
32	0.3190	0.2115	0.1075	0.3450	0.1335	.....	.....
100	0.4338	0.2210	0.2128	0.3410	0.1200	0.4090	0.1808

* $FeSO_4$ in contact with soil suspensions 24 hours before addition of $Ca(OH)_2$.

† $Ca(OH)_2$ present with soil-$FeSO_4$ suspensions one hour before addition of Na_2CO_3.

‡ Over recoveries from $FeSO_4$ additions to soil suspensions.

to show the effect of excesses of $Ca(OH)_2$ upon the solubility of SO_4 in lime-water solutions and in aqueous soil-lime suspensions. The calcium sulfate was made by addition of H_2SO_4 to aqueous solutions of chemically pure $CaCl_2$. A constant charge of 500 gm. of soil was used as before. The $CaSO_4$ additions were made as aliquots equivalent to 0.0735 gm. $BaSO_4$ per 500-cc. aliquot. The excesses of $Ca(OH)_2$ were added in quantities which represented equivalences of 8, 16, 24, 32, and 100 tons of CaO per 2,000,000 pounds of soil. The results of table 7 give the respective totals of sulfate added, the sums of the addition constant and the impurity variables. The recoveries from solutions and $Ca(OH)_2$ excesses alone and with soil are given, together with gram and per cent deviations from theoretical. With increase in charge of $Ca(OH)_2$ in the system $Ca(OH)_2$–$CaSO_4$–H_2O there was found a progressive increase in recovered sulfates, but a progressive increase also in the amounts undissolved. These

unrecovered amounts ranged between 0.0123 gm., or 14.4 per cent, for the 8-ton addition and 0.0783 gm. or 34.8 per cent, for the 100-ton addition. Since all of the lime-water solutions were of equivalent concentration in the absence of soil, it is apparent that the bulk of solid-phase $Ca(OH)_2$ is of more import than the concentrations of the solution phase.

In the soil suspensions, the decreases in sulfate recoveries were still more extensive. Even with the water-soluble sulfates of the soil to draw from the recovery of the $CaSO_4$ from the no-lime control was only 81 per cent of that added. The minimum addition gave a recovery practically identical to the amount of $CaSO_4 \cdot 2H_2O$ added, though but 84.2 per cent of that added as sulfate plus $Ca(OH)_2$ impurities. Increase to the 16-ton rate caused a decrease in recovery, i.e., only 19.5 per cent of the total addition. The 24-, 32-, and 100-ton additions gave the still lower percentage recoveries of 6.2, 4.2, and 2.7 for respective possibilities.

TABLE 7

Influence of $Ca(OH)_2$ additions upon the recovery of SO_4 from an aqueous solution of $CaSO_4$ and from the same solution in contact with a constant soil suspension (experiment 5)*

CaO equivalent per 2,000,000 lbs. of soil	$BaSO_4$ equivalent of calcium sulfate plus $Ca(OH)_2$ impurities	$BaSO_4$ from 500 cc. aliquot		Deviation from theoretical			
		Lime plus $CaSO_4$ solution only	Lime, $CaSO_4$ solution and soil	Lime plus $CaSO_4$ solution only	Lime, $CaSO_4$ solution and soil	Lime and $CaSO_4$ solution only	Lime, $CaSO_4$ solution and soil
tons	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	*per cent*	*per cent*
None	0.0735	0.0735	0.0595	.....	−0.0140	.....	−19.0
8	0.0855	0.0732	0.0720	−0.0123	−0.0135	−14.4	−15.8
16	0.0975	0.0785	0.0190	−0.0190	−0.0785	−18.5	−80.5
24	0.1095	0.0895	0.0068	−0.0200	−0.1027	−18.3	−93.8
32	0.1215	0.0916	0.0051	−0.0299	−0.1164	−24.6	−95.8
100	0.2255	0.1470	0.0161	−0.0785	−0.2194	−34.8	−97.3

* Freshly precipitated from aqueous $CaCl_2$ solution—constant of 0.0735 gm. $BaSO_4$ equivalent.

Experiment 6. Influences of calcium and magnesium hydrates and carbonates upon SO_4 solubility, with and without soil

In earlier lysimeter investigations (5,7) it was found that increased additions of both MgO and $MgCO_3$ caused increases in the outgo of sulfates derived from soil and rainfall. The same finding was later obtained (8) when soluble sulfate and elementary sulfur additions were made. Differing from equivalent treatments of CaO, increases in both $CaCO_3$ and limestone were followed by no depressive effects upon sulfate leachings. In view of those findings the oxides of calcium and magnesium were compared with the corresponding carbonates as to their influence upon the retention of sulfates by the soil of experiments 1-5, which was also used in the above cited lysimeter investigations. The four materials were used in amounts chemically equivalent and at the three rates

used in the lysimeter investigations. Uniform charges of 500 gm. of soil and a dissolved $FeSO_4$ constant of 0.2695 gm. $BaSO_4$-equivalence per 500 cc. were used in 4-liter suspensions of soil and alkali-earths. The recoveries from the four series with and without soil are given in table 8—each result being the average of duplicate determinations upon 500-cc. aliquots.

The recoveries from the $FeSO_4$ additions to the three $Ca(OH)_2$ charges without soil are fairly close. All were less than the amount added in the form of $FeSO_4$, the compensating factors of decreased solubility and increased sulfate impurities being in effect. But, when soil was added there followed a very extensive decrease in sulfate recovery from both 32-ton and 100-ton additions. The difference between the 8-ton and 100-ton recoveries amounted to 0.2605 gm. $BaSO_4$ equivalent.

TABLE 8

Comparison of $Ca(OH)_2$, $CaCO_3$, $Mg(OH)_2$ and $MgCO_3$ additions upon the solubility of SO_4 radical in $FeSO_4$ solution with soil suspensions, (experiment 6)*

CaO equivalent per 2,000,000 pounds of soil	$BaSO_4$ precipitate from 500 cc. aliquots of $FeSO_4$ solution and additions of alkali-earths with and without soil							
	$Ca(OH)_2$		$CaCO_3$		$Mg(OH)_2$		$MgCO_3$	
	After 24 hours contact without soil	After 24 hours contact with soil	After 24 hours contact without soil	After 24 hours contact with soil	After 24 hours contact without soil	After 24 hours contact with soil	After 24 hours contact without soil	After 24 hours contact with soil
tons	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*
8	0.2360	0.2760	0.2773	0.3092	0.2550	0.3135	0.2664	0.3218
32	0.2385	0.0230	0.2755	0.3155	0.2355	0.3005	0.2735	0.3370
100	0.2400	0.0155	0.2695	0.3594	0.2020	0.3100	0.2910	0.3664

*$BaSO_4$ equivalent of 500 cc. of aqueous $FeSO_4$ solution, 0.2695 gm.

On the other hand, the three corresponding $CaCO_3$ additions not only gave concordant recoveries equivalent to, or greater than, the sulfate added in solution in the absence of soil, but they also gave increases above the additions in all cases where the soil mass was present. Thus, the increasing charges of $CaCO_3$ either caused the formation of additional soluble sulfates or decreased the soil's tendency to retain sulfates.

In the case of the MgO addition to $FeSO_4$ solutions without soil, the bulk of undissolved light oxide exhibited a more repressive action than that shown by the excess of $Ca(OH)_2$. In no case was the recovery equivalent to the addition of soluble sulfate. The repression was even more marked because of the smaller amount of sulfate impurities in the MgO and the more marked decrease from the 0.2695 gm. constant, the decrease being, therefore, more in progression, as well as in corresponding totals. The decreased recovery resulting from increase in charge of MgO was chargeable to the sulfate addition, rather than the sulfate impurities of the magnesium oxide. This was determined by the proportionate recoveries of 0.0015 gm., 0.0030 gm. and 0.0068 gm. $BaSO_4$ from MgO charges of 5, 10, and 20 gm., respectively.

However, the introduction of soil was followed by an increase above the 0.2695 gm. constant, rather than the decrease shown by the $Ca(OH)_2$-soil admixtures. It is evident, therefore, that the increase in hydroxyl-ion concentration caused by the $Mg(OH)_2$ produced a different effect from that caused by the hydroxyl-ion increase induced by $Ca(OH)_2$ in the soil suspensions. The concentration of $Mg(OH)_2$, however, was far less than that of $Ca(OH)_2$.

The use of equivalent amounts of hydrated $MgCO_3$ at the three rates, without soil, gave recoveries approximating, or exceeding, the constant addition of 0.2695 gm. $BaSO_4$ equivalent. Where the 500-gm. constant of soil was introduced the recoveries were in all cases in excess of the sulfate addition, and considerably in excess of corresponding recoveries from the respective equivalents of MgO. In harmony with the sulfate recoveries afforded by the several treatments in the lysimeters (7, 8), the $MgCO_3$ proved to be most active in causing the soil to release sulfates to aqueous extractions.

Experiment 7. Influence of aeration and incidental agitation upon tendency of excesses of $Ca(OH)_2$ to inhibit recovery of SO_4

In the discussion of data of experiment 3, mention was made of the possible occlusive action which might be attributed to the small amount of hydrated ferric oxide derived from the ferrous sulfate, in case of its oxidation. This point was considered further. Three charges of $Ca(OH)_2$ were added to 400-cc. portions of $FeSO_4$ in 500-cc. flasks and the flasks connected en train. The CaO equivalences of the three charges are given in table 9. In order to permit observation of color changes, no soil was added to the three charges of $Ca(OH)_2$. Air was drawn through an aqueous guard solution and into the three flasks with such rapidity as to insure constant suspension of the charges during a 24-hour period. The 100-cc. aliquots were then withdrawn and sulfates determined, in parallel with 500-cc. aliquots from a comparable series of larger volume. The larger containers of the parallel series were shaken each half hour for 7 hours and permitted to stand overnight. The results are given in table 9.

Upon settling, all three clear supernatant liquids from the aspirated mixtures were free of iron. A yellowish color soon appeared in the hydrate precipitate of minimum treatment in the first flask in the series. No such color was observed in the two larger additions. It seemed probable, therefore, that the ferrous oxide from the $FeSO_4$ had been converted into the hydrated ferric oxide in all three flasks and that the larger bulk of white hydrate was sufficient to mask the amount of hydrated ferric oxide derived from the ferrous sulfate addition. Additions of freshly precipitate hydrated ferric oxide were therefore introduced into the largest lime suspension in the 500-cc. flask, which was then sealed. A yellowish color prevailed at first, as in the case of the minimum charge after aspiration. This fawn color faded gradually, however, and after one week had entirely disappeared. The point arises whether this change is to be attributed to chemical or physical causes, or to a combination of the two.

Because of the small occurrence of silica, and that most probably as calcium silicate, the small occurrence of insoluble magnesium oxide, and the large active mass of $Ca(OH)_2$, any possible insoluble double salt responsible for SO_4 precipitation would probably be one formed by calcium-iron or calcium-aluminum combination. It will be shown that insoluble ignited Fe_2O_3 undergoes considerable hydration when suspended in solutions of $Ca(OH)_2$. It therefore seems hardly probable that the removal of both Fe and SO_4 from solution was caused by the formation of an insoluble colorless precipitate, calcium-iron sulfate. It seems more plausible to assume that the reddish hydrated oxide particles are masked while serving as nuclei for a progressive deposition of $Ca(OH)_2$ of fineness equivalent to, or approaching, the colloidal state. It may be assumed that both experimental conditions, minimum of contact with maximum agitation and maximum of contact with minimum agitation tend to produce greater dispersion—finer and finer subdivision, i.e. increase in both colloidal state and

TABLE 9

Sulfate recovery from aqueous solutions of $FeSO_4$, as influenced by additions $Ca(OH)_2$ with and without aeration (experiment 7)

CaO ADDITIONS, AS HIGH CALCIC COMMERCIAL LIME PER 500 CC.	$BaSO_4$ EQUIVALENT IN 500 CC.			$BaSO_4$ PRECIPITATE FROM 500 CC. ALIQUOTS AFTER 24 HOURS CONTACT OF $FeSO_4$ SOLUTION WITH LIME			
	Added as $FeSO_4$ in solution	As impurities in lime charge	Total	Periodic agitation and no aeration		Constant agitation and aeration by means of aspiration	
				Found	Unrecovered	Found	Unrecovered
gm.	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*
0.8000	0.2650	0.0135	0.2785	0.2360	0.0425	0.2090	0.0695
2.2857	0.2650	0.0540	0.3190	0.2385	0.0805	0.1660	0.1530
7.1428	0.2650	0.1688	0.4338	0.2400	0.1938	0.1940	0.2398

extreme subdivision approaching that state. With its great surface exposure, hydrated iron oxide would attract sufficient of such finely divided material, thereby becoming covered to the point of loss of its inherent color. Again, under the dynamic conditions of saturated solution over large excesses of solid-phase $Ca(OH)_2$ the continuous passage of the solid phase hydrate into solution phase and the reciprocal precipitation of $Ca(OH)_2$ from solution phase into solid phase may cause cumulative deposition of the white hydrate over the yellow surface of the hydrated ferric oxide, causing the yellow to be masked—time and agitation both tending to hasten the masking effect.

The analyses of table 9 show incomplete recovery of the sulfate present in each $Ca(OH)_2$ suspension, for both periodic agitation without aeration and constant agitation and aeration through aspiration. With increase in mass of solid phase $Ca(OH)_2$ the amounts of unrecovered SO_4 also increased. The unrecovered fractions of sulfates were consistently greater in the aspirated series. The more thorough agitation effected by the steady stream of air which bubbled through the suspensions is most probably the cause of the differ-

ences between the two series. For, with limited periodic agitation, without aeration, it was found that lapse of time caused increases in the amounts of unrecovered sulfate. It is quite possible, however, that with progress of time, more and more of the solid-phase $Ca(OH)_2$ passes into colloidal state, by which change its absorptive properties are naturally increased. Both conditions—continued contact of lime with excess of water, and periodic agitations and shorter period of time with continuous agitation—would tend to effect greater dispersion and augmented absorptive properties. Both conditions do effect increased absorption. It therefore appears that change in physical condition of lime suspensions, is the cause for increased calcium sulfate absorption and this change may be induced in the main either by time or agitation.

Experiment 8. Residual effect of $Ca(OH)_2$ upon subsequent additions of soluble sulfate to suspensions of ignited and unignited soil

The data of table 2 show that the large bulks of solid-phase $Ca(OH)_2$ cause an absorption of the sulfate radical, *per se*. The data of table 3 show that, to a minor extent, the mass of acid soil also removes SO_4 from solution. Table 3 and 4 show further that the absorptive property of the soil mass was greatly increased upon the addition of the excess of lime. It appears further, from tables 5 and 6, that the conversion of the excess of $Ca(OH)_2$ into $CaCO_3$ nullified the ability of the soil to retain the sulfate which was added before, or simultaneously with, the introduction of lime. Experiment 8 was accordingly planned to determine the residual effect of $Ca(OH)_2$ upon the retentive activities exerted by soil and its ignited residue for sulfate additions before and after carbonation by means of CO_2. It was thought that dehydration of hydrated siliceous and other materials, conversion of all ferrous and ferric components into ferric oxides, destruction of colloidal complexes and elimination of organic matter, through the agency of intense heat would give some indication of the reasons for the marked increase in a soil's retentive properties for sulfate when it is treated with an excess of $Ca(OH)_2$.

The following conditions were therefore imposed: Constant charges of 500 gm. of soil, or its ignited residue, and 20.0 gm. of high-grade commercial $Ca(OH)_2$ and a constant volume of 2,000 cc. of distilled water were used. The 500-gm. charges of soil were ignited at 900°C. for three hours in a large electric furnace. The soil and residue suspensions and $Ca(OH)_2$ additions were agitated every half hour for seven hours and permitted to stand overnight before the addition of Na_2SO_4 to six of the eight suspensions by means of a 25-cc. volume of an aqueous solution. They were agitated hourly seven times, during the second day, and again permitted to stand overnight. Aliquots of 500 cc. were withdrawn for titrations and $BaSO_4$ determinations. Aqueous extracts of soil and ignited soil were made as controls against the same suspensions plus Na_2SO_4. At the end of the first overnight period CO_2 was passed into one of the soil-$Ca(OH)_2$ suspensions, and one ignited residue until all $Ca(OH)_2$ was converted to $CaCO_3$.

The sulfate recovery from the ignited control was more than twice that obtained from the untreated soil after extraction for 48 hours, and also after 16 days. On the other hand, the two sulfate recoveries from the fortified ignited residue were only 92.3 per cent and 93.5 per cent of the sulfate addition, while those from the Na_2SO_4-soil control were 4 per cent and 6 per cent in excess of the added sulfate. The addition of $Ca(OH)_2$ had a very decided effect upon

TABLE 10

Residual effect of $Ca(OH)_2$ upon subsequent additions of soluble sulfate solution to suspensions of ignited and unignited soil* after periods of 48 hours and 16 days (experiment 8)*

AQUEOUS SUSPENSIONS OF	ALKALINITY 500 CC. ALIQUOTS TERMS OF 0.5 NORMALITY AFTER		SULFATE CONTENT OF AQUEOUS EXTRACTIONS, AS $BaSO_4$ EQUIVALENT PER 500 CC. ALIQUOTS					
			After 48 hours†			After 16 days		
	48 hours	16 days	Found	Deviation from respective controls		Found	Deviation from respective controls	
				Found	Basis of Na_2SO_4 addition		Found	Basis of Na_2SO_4 addition
	cc.	*cc.*	*gm.*	*gm.*	*per cent*	*gm.*	*gm.*	*per cent*
Soil	0.6	1.6	0.1005	.....	.....	0.1075	.....	.....
Ignited soil	0.8	1.0	0.2234	0.1229	.....	0.2176	0.1101	.....
Soil plus Na_2SO_4	0.6	1.5	0.3705	0.2700	104.0	0.3830	0.2755	106.1
Ignited Soil plus Na_2SO_4	0.8	1.0	0.4630	0.2396	92.3	0.4603	0.2427	93.5
Soil, Na_2SO_4 and $Ca(OH)_2$	37.4	33.5	0.1405	−0.2300	−88.6	0.0183	−0.2647	−102.2
Ignited soil, Na_2SO_4 and $Ca(OH)_2$	37.4	19.7	0.0832	−0.3798	−146.3	0.0033	−0.4570	−176.0
Soil, Na_2SO_4, $Ca(OH)_2$ plus CO_2	4.4	‡	0.3130	−0.0575	−22.2	0.4215	0.0385	14.8
Ignited soil, Na_2SO_4, $Ca(OH)_2$ plus CO_2	9.9	2.8	0.4145	−0.0485	−18.7	0.4987	0.0384	14.8

* 20 gms. commercial hydrate to 500 gm. of soil in 2,025 cc. distilled water.

† Na_2SO_4 additions equivalent to 0.2596 gm. $BaSO_4$ per 500 cc. aliquot made 24 hours after making suspensions and immediately after conversion of excess of $Ca(OH)_2$ into $CaCO_3$.

‡ Uncertain endpoint because of instability of indicator in colored supernatant.

the removal of sulfate from solution in both soil and ignited-residue suspensions, the effect increasing with time. The differences between the recoveries from the fortified-soil suspension and those from the 3-component suspension, soil-Na_2SO_4-lime, showed removals of 88.6 per cent and 102.0 per cent of the sulfate addition from solution phase, as a result of the influence exerted by the lime during the two periods. But the absorption exerted by the ignited residue and lime suspension was still more extensive for both periods, amounting, respectively, to nearly 1.5 times and over 1.75 times the amount added as Na_2SO_4. The 48-hour and 16-day sulfate extraction from the suspension of ignited

residue, plus both Na_2SO_4 and lime, were, respectively, only 82.8 per cent and 3.1 per cent of corresponding recoveries from soil alone, and only 37.2 per cent and 1.5 per cent of corresponding extractions from the unfortified ignited soil. The sum of aliquot recovery from the ignited residue treated with Na_2SO_4 and $Ca(OH)_2$ and the aliquot fraction of added sodium sulfate was 0.1302 gm. less than the recovery from the ignited residue treated with sulfate without lime for the 48-hours period. For the 16-day period a corresponding discrepancy of 0.1974 gm. was obtained. With continued contact of ignited residue plus Na_2SO_4 with excess of lime the sulfate recovery was practically nil. It is thus apparent from the 48-hour-contact data that after the changes incident to burning, the added lime was responsible for completely removing from the solution phase not only all of the added sulfate, but also 0.1202 gm. of that dissolved from the original unlimed ignited residue by each 500-cc. aliquot. But the 16-day period served to eliminate all but 0.0033 gm. of the 500-cc. aliquot total of 0.5889 gm. supplied by ignited soil, $Ca(OH)_2$ content, and Na_2SO_4 addition.

Inspection of the soil-sulfate-lime suspension showed it to be very different from the corresponding ignited-residue suspension. A part of the ignited soil had been converted to coarse red granules, undisintegrated by the subsequent suspension and agitation. But the more granular part was capped by a large amount of a reddish flocculant interspersed throughout the lighter upper zone of lime, while no such occurrence was noted in the soil suspensions. After several days contact and settling overnight following agitation, the unignited soil plus sulfate and lime had a depth of 1.87 inches in the 4-liter bottles, while the ignited residue containing sulfate and lime was 2.87 inches deep. It will be noted also that though both soil and ignited residue suspensions decreased the $Ca(OH)_2$ concentrations in the interval of fourteen days, the ignited soil was very much more effective in this respect.

The passage of CO_2 into admixtures of sulfate and lime, with soil and with ignited soil, caused a decided difference in the amounts of sulfate held by the two solids against the 48-hour extraction. The recovery from the soil fortified with Na_2SO_4 was 2.25 times that from soil with the same sulfate addition plus lime. But the recovery from the fortified ignited residue was five times that obtained from the same residue in contact with $Ca(OH)_2$. In spite of a still further addition of sulfate through introduction of the sulfate impurities of the calcium hydrate, the recoveries from the two carbonated media after forty-eight hours were not so great however as those obtained from the respective controls fortified with Na_2SO_4 in the absence of lime. The residual effect of the added hydrate still appears to be in some evidence, therefore, at the conclusion of the first period of contact. This residual effect had disappeared entirely, however, after fourteen days for both soil and ignited residue, each of which gave recoveries about 15 per cent above the respective controls.

The characteristic flocculation and color of soil mass, mentioned in discussing the ignited residue suspensions containing Na_2SO_4 and $Ca(OH)_2$,

disappeared entirely after conversion of hydrate to carbonate. Likewise the depth of the columns were the same, 1.62 inches, as compared to depths of 1.87 inches and 2.87 inches, for soil and ignited soil, prior to the passage of CO_2.

The readiness with which the ignited iron underwent hydration and flocculation in the $Ca(OH)_2$ solutions was most striking. The distinct increase in retentive power of the soil after ignition, coincident with the presence of the mass of hydrated iron oxide, the rapid precipitation of the iron upon treatment with CO_2, and the coincidental loss of absorptive power suggest rather forcibly that the hydrating effect exerted by $Ca(OH)_2$ upon ferric and probably aluminic compounds in the soil is one, if not the main, cause for the retention of soluble sulfates by the soil mass. Silica and silicate complexes also may have been of some effect. Further work is planned to determine more fully the extent to which iron, alumina and silica may be, singly or jointly, responsible for the observed absorption phenomena.

CHANGE IN $Ca(OH)_2$ CONCENTRATION AS INFLUENCED BY SUSPENSIONS AND BY TIME

Both soil and ignited-soil controls, and the same controls plus Na_2SO_4, gave somewhat greater alkalinity indications in the 500 cc. aliquots after sixteen days. The reverse was true, however, for the lime additions to both soil and ignited residue. While the decrease in alkalinity was very positive in the soil suspension it was still more impressive—equivalent to 47.3 per cent—in the ignited residue suspension. A titration made nineteen days later showed a still further decrease to 30.2 per cent of that found after the first 48-hour contact. The decrease in $Ca(OH)_2$ could hardly be attributed to continued reaction between insoluble acid components of the soil and $Ca(OH)_2$ during the 48-hour preliminary period. In the ignited residue, eradication of acid reacting materials was still more positive. However, the ignited residue was still more effective in decreasing the $Ca(OH)_2$ concentrations in the aqueous suspensions. Corresponding data in tables 3 and 4 show that with increase of time there is a definite decrease in $Ca(OH)_2$ concentrations of the aqueous extractions from similar soil suspensions. It is apparent therefore that the $Ca(OH)_2$ exerts a progressive hydrating action upon soil. The hydration of the ignited residue was still greater. The products of the hydrating action have the property of absorbing $Ca(OH)_2$ as well as $CaSO_4$. With marked increase in absorptive properties, there was readily discernible a considerable increase in hydrated Fe_2O_3 which resulted from contact of $Ca(OH)_2$ with the ignited residue. From this it would appear that the hydrated iron oxide was responsible, in part at least, for progressive adsorption of $Ca(OH)_2$.

FURTHER SULFATE RECOVERIES FROM RED FLOCCULATE OF IGNITED SOIL AND LIME SUSPENSIONS

Since the preparation of this manuscript and its approval for publication a contribution by Lichtenwalner, Flenner and Gordon (4) has thrown considerable

light upon the problem more especially the findings of tables 10 and 11. These investigators found a definite adsorption of the $CaSO_4$ molecule by ferric and aluminic hydrogels obtained by ammoniacal precipitations. It was also found that some of the adsorbed SO_4 radical could be recovered by successive aqueous extractions.

Nineteen days after the end of the 16-day period of contact given in table 10, a 600-cc. volume of the supernatant and upper part of the suspension of the fortified ignited residue and $Ca(OH)_2$ was syphoned off into a 600 cc. cylinder. After settling, the upper 550 cc. of $Ca(OH)_2$ solution and suspension was withdrawn and the lower 50 cc. discarded. Of this 550-cc. volume, the upper 365-cc. portion was clear $Ca(OH)_2$ solution and the lower 185-cc. fraction was reddish lime-impregnated flocculate. The flocculate was thrown upon a

TABLE 11

Additional sulfate recoveries and alkalinity determinations from a portion of the ignited-residue-lime suspension fortified with Na_2SO_4

LAPSE SINCE PREVIOUS EXTRACTION	0.5 *N* VALUE PER 500 CC. EXTRACT	$BaSO_4$ PER 500 CC. EXTRACT
	cc.	*gm.*
19 days	11.3* †	0.0473* ‡
2 hours	5.3	0.0293
2 hours	4.5	0.0260
1.25 hours	4.5	0.0259
1.50 hours	3.5	0.0240
Overnight	4.6	0.0286
1.50 hours	3.9	0.0232
1.25 hours	4.0	0.0202
2.50 hours	3.6	0.0210
Overnight	4.0	0.0295
	49.2	0.2730

Residual sulfate in flocculate obtained by Na_2CO_3 fusion 0.3690 gm.

* Calculated from determination on 550 cc. volume, inclusive of flocculate.

† Corresponding determinations 35 days previous 19.7 cc., 37 days previous 37.4 cc.

‡ Corresponding determinations 35 days previous 0.0033 gm., 37 days previous 0.0832 gm.

Büchner filter and washed with 100 cc. of distilled water. The residue was then returned to the stoppered cylinder and subjected to the successive extractions and determinations specified in table 11.

The reddish flocculate was analyzed after the tenth extraction shown in table 11. The entire flocculate weighed 36.9155 gm. Of this, 2.4610 gm., or 6.67 per cent, was accounted for by CaO; 2.3060 gm., or 6.25 per cent, was due to strong-HCl soluble Fe_2O_3-Al_2O_3-P_2O_5 and 26.4093 gm., or 71.54 per cent, was SiO_2. There was therefore about 15 per cent of acid insoluble Fe_2O_3-Al_2O_3 in the more inactive granules. Of the total SO_4 present from $Ca(OH)_2$ impurities and Na_2SO_4 addition in the full residue after ignition of soil, 0.0865 gm. had been removed by the two extractions shown in table 10. There was left, therefore, 1.8751 gm. in the entire charge accounted for by ignited residue and Na_2SO_4

and disregarding SO_4 impurities in the full charge of lime before the two extractions of table 10. Including the sulfate impurities, there was an initial sulfate occurrence of 2.2138 gm. $BaSO_4$ equivalence. At the beginning of the ten extractions of table 11 the $BaSO_4$ equivalence present was therefore 2.1273 gm. The sulfates unrecovered by the aqueous extracts impregnated with $Ca(OH)_2$ gave a $BaSO_4$ equivalence of 0.3690 gm. Of the amount present a total $BaSO_4$ equivalence of 0.6420 gm., or 30.1 per cent, was found in the more hydrous flocculate suspended in 185 cc. volume of $Ca(OH)_2$ solution. The 0.3690 gm. residue after the extractions was 1.35 times more than the total amount recovered by the ten successive aqueous extractions. The total bulk of lime and insoluble residue, including the portion subjected to the ten additional aqueous extractions, amounted to 715-cc. The unextracted 530-cc. portions contained most of the granular oxides and lime and it was much more compact than the upper 185 cc. used in obtaining the ten extractions of table 11. It did, however, contain a considerable quantity of the more flocculant material which furnished the 185 cc. volume of successively extracted flocculate. It is thus apparent that 30 per cent of the sulfate was occluded by the reddish flocculate made up of $Ca(OH)_2$ and hydrated oxides of iron and aluminum and silica, which represented 25 per cent of the bulk of the suspension as it stood in the cylinder. Upon filtration, however, the flocculate was compacted to a volume of about 35 cc. On the other hand, the more granular fraction was changed but little in bulk by filtration. It is not established what part of the determined sulfate adsorption is to be attributed to either of these several components.

EXPERIMENT 9. INFLUENCE OF $Ca(OH)_2$ UPON RAIN WATER CONCENTRATIONS OF SULFATES

In the report of previous lysimeter experiments (7, 8) it was pointed out that the leachings from the heavily limed tanks were of lower SO_4 concentration than the same waters prior to their movement through the surface soil. Since the sulfate concentrations of rain water were much less than those of the several sulfate solutions used in the present experiment, it seemed desirable to impose some of the previous contact conditions with rainfall concentration of sulfates. Accordingly, the lime treatments were made to rain water alone and to rain water and soil. As controls, $BaSO_4$ determinations were made upon rain water, distilled-water extractions of $Ca(OH)_2$, and rain water extractions of soil alone. Five hundred grams of soil, 23.22 gms. of high grade commercial lime, and 3500 cc. of rain water were used. The lime charge carried 0.3910 gm. of $BaSO_4$ equivalent. The containers were agitated several times during the afternoon when charges were introduced. After standing overnight undisturbed, they were agitated hourly for seven hours during the following day and again permitted to stand overnight, after which 1-liter aliquots were withdrawn for titrations and $BaSO_4$ determinations. The residues were then permitted to

stand for fourteen days, being agitated once each day during that interval. The results obtained from the five conditions named are given for both periods of contact in table 12.

By subtraction of the amount of $BaSO_4$ found in one liter of rain water from the rain water extract of the burnt lime, a gain of 0.0780 gm. appears for the 36-hour contact. This increase fell 0.0337 gm., or 26.2 per cent, below the computed total amount present. The 0.0817-gm. recovery from the burnt lime by the parallel distilled-water extraction amounted to 73.1 per cent of that present, or a discrepancy of 26.9 per cent. This agrees closely with the corresponding deficiency obtained in the rain-water extraction, although there was an appreciable difference between the $Ca(OH)_2$ concentration of the two solutions. The corresponding data for the 16-day interval showed but little

TABLE 12

Influence of $Ca(OH)_2$ upon the sulfate concentration of rain water alone and with soil† suspensions (experiment 9)*

AQUEOUS SUSPENSIONS	ALKALINITY OF 1,000 CC. ALIQUOTS, TERMS OF 0.5 NORMALITY AFTER		SULFATE CONTENT OF RAIN WATER EXTRACTS AS $BaSO_4$ EQUIVALENT PER LITER‡					
			After 36 hours			After 16 days		
			Found	Variation from		Found	Variation from	
	36 hours	16 days		Actual	Theoretical		Actual	Theoretical
	cc.	*cc.*	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*
Rain water only	0.6	0.6	0.0168	.....	.....	0.0168	.....	.....
Rain water and lime	89.6	90.6	0.0948	0.0780	−0.0337	0.1031	0.0863	−0.0254
Distilled water and lime	88.7	89.4	0.0817	−0.0131	−0.0468	0.0881	−0.0150	−0.0404
Rain water and soil	0.6	1.9	0.1625	.....	.....	0.2005	.....	.....
Rain water, soil and lime	81.0	72.8	0.0317	−0.1308	−0.2425	0.0238	−0.1767	−0.2884

* 20 gm. CaO per 3500 cc.

† 500 gm.

‡ $BaSO_4$ per liter on basis of total SO_4 content of lime charge, 0.1117 gm.

variation from those of the shorter period. For the 36-hour and 16-day intervals the rain-water extractions of soil alone contained, respectively, nearly ten times and about twelve times the sulfate content of the rain water. These proportions are many times the reverse of the proportion which obtained when rainfall leached through this same soil in the lysimeters. The addition of hydrated lime to the rain water and soil caused a decrease of 80.5 per cent from the recovery obtained in the absence of lime after 36 hours, or a decrease of 81.1 per cent of the theoretical, as represented by the sum of the soil extraction and the amount which would have been present in 1 liter if all SO_4 had been dissolved from the lime charge. The corresponding differences obtained after 16 days were still greater. The discrepancy between the depressive effect

exerted by the excesses of lime upon the rain water during its passage through the limed surface soil and the corresponding effect upon the rain-water extractions is most probably due to the better opportunity afforded for solution of the sulfate impurities of the lime under the imposed laboratory conditions.

COMPARISON OF EXTRACTIONS AND NATURAL LEACHINGS AS MEANS OF SULFATE RECOVERIES

Since the soil used in the sulfate extractions was also used in the 5-year lysimeter studies (7) of sulfate outgo from surface soil alone, an unusual opportunity is afforded for quantitative comparisons between the imposed conditions of agitation and extraction by the large proportion of water to soil and natural leachings from lysimeters. In so far as we are aware, this comparison has not been made. One possible vitiating factor in the comparison is that the moist soil was brought to an air-dry condition and maintained in that state during a 5-year interval. It is possible that such a maintained change may effect the colloidal material of the soil and thus influence its retentive properties. Assuming such to be the case, however, it is quite possible that the agitation of soil with the large proportion of water would quickly cause reversion of the colloidal material to the condition which obtained prior to its being brought to the air-dry state.

The sulfate precipitation per acre surface during the 5-year interval amounted to 214.7 pounds of S. The soil leachings from the 256.0-acre-inch precipitation during that period would therefore have had for its leaching content 214.7 pounds of sulfur—if the rainfall concentration of sulfates were not altered by passage through the layer of soil—in addition to the amount of sulfate derived from a total soil sulfur content of 0.0326 (SO_3, 0.0815) per cent. But the average $BaSO_4$ equivalence of 0.0394 gm. per liter (8) in the total 5-year leachings of 716.4 liters from the untreated control tank gave a total sulfate sulfur outgo of only 175.8 pounds, or 38.9 pounds less than the sulfur brought to the soil by rain water during the same period. As against this outgo in the lysimeter leachings, the 0.1005-gm. $BaSO_4$ determination (table 10) represents one-fourth the water-soluble sulfate extracted from 500 gm. of soil which had been kept in air-dry conditon for nearly six years. This recovery of 0.4020 gm. $BaSO_4$ (0.0551 gm. S) from 500 gm. of soil is equivalent to 0.011 per cent, or 220 pounds of sulfate sulfur per 2,000,000 pounds of soil. Thus, by a 48-hour contact, with periodic agitation and extraction a 0.0326 per cent total sulfur content yielded sulfates at the rate of 220 pounds of sulfur per 2,000,000 pounds of soil. But from the same sulfur content, plus 214.7 pounds of rain-water sulfate sulfur, the 5-year leachings totaled only 175.8 pounds. There is thus a difference of 44.2 pounds in favor of the aqueous extractions, which demonstrates the intensity of laboratory extractions—for sulfates from this loam, at least—as compared to natural leachings.

A parallel may also be made between the recovery of SO_4 from $FeSO_4$ additions in the laboratory extractions and the sulfate sulfur leached from the same

soil in the lysimeters. In both cases the sulfate addition supplied S at the rate of 1000 pounds per 2,000,000 pounds of soil. In both cases, also, the Fe of the $FeSO_4$ was retained by the soil. In the extractions, the sulfate recovery was in the form of $CaSO_4$, while in the lysimeter leachings it was accounted for in most part by native calcium and also by magnesium. In the unsupplemented $FeSO_4$ tank, the 1000-pound sulfate sulfur addition yielded 934.6 pounds (8), or 758.8 pounds more than the outgo from the no-treatment tank, during the 5-year period of rainfall leaching. Of this 5-year total recovery of 934.6 pounds, 534.3 pounds were leached by the subnormal precipitation of 37.69 inches during the first year. The leachings for the succeeding 4 years were 180.9 pounds, 109.3 pounds, 67.7 pounds, and 42.4 pounds. From the corresponding $FeSO_4$-solution-additions the 0.2350 gm. $BaSO_4$ equivalent, obtained in the 500-cc. aliquot after 24-hours extractions of 500 gm. of soil with 2,000 cc. of water, was 0.0300 gm. less than the amount added. This extraction-recovery represents 886.8 pounds per 2,000,000 pounds of soil, or practically the same recovery, 892.2 pounds, obtained during the first four years in the lysimeter leachings. It should be remembered, however, that the lysimeters received as a result of the 4-year composite of rainfall, 175.8 pounds of soluble sulfate-sulfur in excess of that added to the laboratory-extracted suspensions.

It is thus apparent that though dissolved $FeSO_4$ and $CaSO_4$ additions were not fully recovered from the acid-soil suspensions by the short-period extractions with periodic agitations, such laboratory treatments were much more intense than natural leachings in the recovery of added soluble sulfates, since the laboratory extractions proved equivalent to four years' leaching in the exposed tanks.

SUMMARY

A study was directed toward the influence of $Ca(OH)_2$ in causing the soil to retain more of native and engendered sulfates and added $FeSO_4$.

Preliminary determinations, with wide range in charges, showed a near-constant proportion of total sulfates in HCl solutions of charges (table 1), and a distinctly decreased recovery of water-soluble sulfate impurities, with increase of solid-phase $Ca(OH)_2$ (table 2).

In equivalence to an 8-ton CaO admixture per 2,000,000 pounds of soil, immediate additions of $Ca(OH)_2$ to aqueous $FeSO_4$-soil suspensions gave decreasing alkalinity and increasing sulfate recoveries for 24-hour, 48-hour, and 16-day intervals of periodic agitation, the recoveries after the two longer periods having been in excess of total additions. With increase of time, the clear supernatant solutions from 32- and 100-ton additions of CaO showed some decrease in $Ca(OH)_2$ concentration and almost complete absence of sulfates (experiment 1, table 3).

The same findings were obtained when the lime additions were not made until after a preliminary period of contact between acid soil and added $FeSO_4$ solution. (Experiment 2, table 4).

After one hour's preliminary agitated contact of soil and $FeSO_4$, the three lime additions were made to sulfates and suspensions agitated hourly for seven hours and left overnight. Sulfates were then determined in the supernatant lime-water solutions and the $Ca(OH)_2$ suspensions converted to $CaCO_3$ by addition of Na_2CO_3. After twenty-four hours, the 8- and 32-ton additions gave sulfate recoveries in excess of the amounts introduced as water-soluble sulfates, while a large increase was obtained also in the 100-ton addition. Fourteen days later the recoveries from all three treatments were still greater, and in excess of added soluble sulfate for all three rates (experiment 3, table 5).

A similar result from conversion of $Ca(OH)_2$ to $CaCO_3$ by means of CO_2 showed the increase in SO_4 recoveries to be due to conditions induced by the presence of $Ca(OH)_2$, rather than to NaOH derived from the $Ca(OH)_2+Na_2CO_3 \rightarrow CaCO_3 + NaOH$ reaction.

Delay of twenty-four hours in the conversion of $Ca(OH)_2$ to $CaCO_3$, by means of Na_2CO_3, showed the same eradication of the precipitative properties caused by $Ca(OH)_2$, and a similar gain in sulfate recoveries, with increase of time after the $CaCO_3$ conversion, which obtained with the shorter period of $Ca(OH)_2$ contact and its earlier conversion to $CaCO_3$ (experiment 4, table 6).

Additions of dissolved $CaSO_4$ were made to similar soil and no-soil suspensions and five excesses of $Ca(OH)_2$ as parallel to the introduction of $CaSO_4$ through the $FeSO_4$-$Ca(OH)_2$ reaction. The addition of the soil caused a marked decrease in dissolved sulfate. The minimum deviation of -15.8 per cent from addition and water-soluble impurities came from the 8-ton CaO treatment, and the maximum of -97.3 per cent from 100 tons (experiment 5, table 7).

In parallel with lysimeter experiments, where equivalent amounts of $Ca(OH)_2$, $CaCO_3$, MgO, and $MgCO_3$ were used, these four materials were added at 8-, 32- and 100-ton rates in $FeSO_4$ solutions, with and without soil. Concordant SO_4 recoveries from the $FeSO_4$ constant and impurity variables were obtained from $Ca(OH)_2$ alone; but the addition of soil showed decrease parallel with increase in $Ca(OH)_2$. A near-constant recovery from the three $CaCO_3$ additions was changed to increase with treatment in the presence of the added soil. A progressive decrease was found in the $FeSO_4$-MgO suspensions, coincident with increased amounts of MgO. This effect disappeared in the $FeSO_4$-MgO-soil suspensions. Proportionate sulfate impurity recoveries from the three charges of MgO without sulfate additions showed the effect of oxide to be upon the added sulfate. $MgCO_3$, alone and with soil, gave increased SO_4 recoveries parallel with increase in the amount of carbonate additions (experiment 6, table 8).

Agitation of six aqueous $FeSO_4$-$Ca(OH)_2$ suspensions, three with periodic agitation and no aeration, and three with constant agitation induced by an aerating current, showed progressive increase in the amounts of sulfates unrecovered for increase in lime charges under both conditions. Each aerated charge showed, however, less sulfate recovery than that shown by its corre-

sponding unaerated parallel. The foregoing result was considered as due to the more favorable conditions for colloidal dispersion and consequent increased absorption by the excesses of $Ca(OH)_2$ rather than to absorptive properties of the small amount of $Fe_2O_3 \cdot nH_2O$ formed from the ferrous sulfate. It was observed that the yellow color caused by such $Fe_2O_3 \cdot nH_2O$ disappeared entirely upon standing. Possible explanations of this phenomenon are advanced (experiment 7, table 9).

Influence of soil structure, or composition, and the occurrence of hydrated ferric and aluminic oxides and silica as causative factors in the absorption of sulfates by the soil during persistence of $Ca(OH)_2$, were considered for two periods in parallels, between soil and soil-Na_2SO_4 suspensions and similar suspensions of ignited soil. After forty-eight hours the unfortified ignited soil gave an SO_4 extraction more than double that of the control. The sulfate recoveries from the fortified control were greater for both periods, however, than those from the fortified ignited residue. The $Ca(OH)_2$ addition was very much more active upon the fortified ignited residue than upon the fortified soil in causing increased absorption and upon formation of $Fe_2O_3 \cdot nH_2O$. Where $Ca(OH)_2$ excesses were converted to $CaCO_3$, both soil and ignited soil lost most of their absorptive properties during the 48-hour period, while all such properties were destroyed during the 16-day period (experiment 8, table 10).

The more flocculant part of the ignited residue suspension was subjected to ten successive aqueous extractions by which continued sulfate recoveries were obtained; but the larger part of adsorbed sulfate was still retained. The more flocculant reddish fraction of the suspension was found to show greater adsorption than the denser fraction.

On continued contact with $Ca(OH)_2$ solutions and excesses of solid phase $Ca(OH)_2$, the soil suspension caused decreased concentration of $Ca(OH)_2$. The same effect was produced with much greater intensity by the ignited soil residues.

Influence of excess of $Ca(OH)_2$ upon rain-water concentrations of sulfate was studied to throw some light upon the paucity of sulfates in the rain-water leachings from the same heavily limed soil in lysimeters. Lime additions to distilled water and rain water gave minus variations from theoretical in both cases after 36-hour and 16-day periods of contact. Soil-$Ca(OH)_2$-rainwater suspensions resulted in still more striking and progressive decreases for the same periods (experiment 9, table 11).

Comparison between sulfate recoveries obtained by agitation and extraction of soil with large proportions of water and those obtained by rainfall leachings showed the extracted sulfates from the air-dried reserve to be in excess of those leached during 4–5 year periods, in spite of the additional soluble sulfate added to the lysimeters by rainfall. This held for both native and added sulfates.

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THE REPLACEMENT OF SOIL POTASSIUM

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In a previous investigation (4) it was observed that finely crushed potassium-bearing rocks in water solutions, treated with manure extract yielded considerable quantities of water-soluble potassium after standing for four months at a temperature of about 25°C. These results were taken as a basis for an experiment in which 500-gm. quantities of soil in quadruplicate were treated with varying amounts of clover hay and medium decomposed manure, and distilled water added for optimum moisture conditions. Two soils of each treatment were sterilized and two were unsterilized. After incubating 10–12 weeks at 25°C. the soils were air dried and water-soluble potassium was determined.

It was found that there was no relation between the carbon dioxide production and the liberation of water-soluble potassium.

The sterilized soils yielded more water-soluble potassium than the soils in which normal biological activities were allowed to take place. Increased applications of organic matter resulted in increased quantities of water-soluble potassium, but the latter increases did not equal the total amount of soluble potassium added in the form of clover hay and manure. This was undoubtedly due to the adsorptive and absorptive powers of the soil which are known to prevent the soluble potassium from going into solution in subsequent water extractions.

A method to determine this absorbed potassium must be developed before the effects of various soil treatments on the liberation of soil potassium can be ascertained quantitatively.

The experiment reported in this paper was planned for that purpose.

The method used involved replacing the exchangeable bases by treatments with neutral salt solutions such as NH_4Cl, $CaCl_2$, etc. This idea is not new. In 1887 Kellner (3) reported that the absorbed potassium of the soil can be replaced completely by repeated leachings with a hot, saturated solution of NH_4Cl, and that only the potassium in solution and in the absorbed form are extracted, that contained in the un-weathered minerals and rocks not being attacked. He further showed by experiments that only soluble and absorbed potassium can be utilized by field peas.

[1] The writer wishes to express his thanks to Dr. P. E. Brown for reading the manuscript.

Very little attention was paid to these important experiments until later. In 1896 Huston and Bartlett (2, p. 91–96) tried a number of solvents for available potassium and phosphorus. As a result of their investigations they came to the conclusion that alkaline NH_4Cl and neutral NH_4Cl were promising solvents for the determination of available potassium.

Not until 1920 was there any extensive work done on the replacement of soil bases with relation to their availability to plants. Hissink (1) carried on some interesting work on exchangeable bases. He reported that all the absorbed potassium is just as available for plants as that in water-soluble forms, and that only the water-soluble and absorbed potassium is replaced by leaching with solutions of neutral salts, such as NH_4Cl, $CaCl_2$, etc.

It is thought that the potassium molecule is held adsorptively by the colloidal complexes of the soil. The replacement method involves a reversible chemical reaction on the adsorbed molecules. This reaction stops at the point of equilibrium between the solution applied and that around the colloidal nucleus. It is evident, therefore, that a single treatment with a neutral salt solution will not replace the total amount of absorbed potassium. The leaching process must be resorted to. Due to the relatively small amount of absorbed potassium present in the soil comparatively few leachings are required.

In this experiment it was found that two extractions replaced about 90 per cent of the total absorbed potassium. These quantities being sufficient for the purpose of this investigation no further leachings were made.

Although the processes involved in this work include surface phenomena which are purely adsorptive, the replacement itself is a chemical reaction—limited, however, to the molecules which form the surface layer of a nucleus possessing colloidal properties. Hence, except for the small amount of water-soluble potassium present in the soil, this reaction does not occur in stoichiometric proportions. Neither is it a purely physical phenomenon. Probably both phases enter into the processes, and since that is the case confusion will perhaps be avoided best by using only the term "absorbed" throughout this paper.

EXPERIMENTAL

The Carrington loam samples treated with clover hay and manure described in the previous investigation (4) were used in this experiment. Normal solutions of NH_4Cl or $CaCl_2$ were first used for replacement purposes. Both solvents were found to give equally good results, but due to the fact that the $CaCl_2$ extracts contained large quantities of calcium to be precipitated the use of this solvent was discontinued.

One hundred grams of the air-dry soil were placed in shaker bottles with 500 cc. of normal NH_4Cl solution and shaken for three hours in the shaking machine. The soil was allowed to settle and the supernatant liquid was decanted, and filtered through the Chamberland Pasteur filters. Most soils would filter

TABLE 1

Replaceable potassium from soil treated with clover hay and manure

SAMPLE NUMBER	TREATMENT (CALCULATED PER ACRE)					NOT STERILIZED					STERILIZED AND KEPT STERILE				
	Manure	$CaCO_3$	Ortho-clase	Acid phos-phate	Clover hay	Average K_2PtCl_6	K	K per acre	K per acre added in form of manure and orthoclase	Increase (+) or decrease (−)	Average K_2PtCl_6	K	K per acre	K per acre added in form of manure and orthoclase	Increase (+) or decrease (−)
	tons	*tons*	*tons*	*pounds*	*tons*	*gm.*	*per cent*	*pounds*	*pounds*	*pounds*	*gm.*	*per cent*	*pounds*	*pounds*	*pounds*
1	Check (soil in field)					0.0113	0.01819	363.8	0	0	0	0	0	0	0
2	Check (at optimum moisture for 10 wks.)					0.0114	0.01835	367.0	0	0	0.0115	0.01851	370.2	0	0
3	8					0.0168	0.02704	540.8	171.2	+2.6	0.0164	0.02640	528.0	171.2	−13.4
4	16	4	40			0.0219	0.03525	705.1	369.4	−31.3	0.0214	0.03445	689.0	369.4	−50.6
5	32	4	40			0.0335	0.05393	1078.7	711.8	0	0.0362	0.05828	1165.6	711.8	+83.6
6	32	4	40	1000		0.0350	0.05635	1127.0	711.8	+48.2	0.0369	0.05940	1188.1	711.8	+106.1
7	32		40			0.0343	0.05522	1104.4	711.8	+25.6	0.0344	0.05538	1107.6	711.8	+25.6
8			40		4	0.0148	0.02382	476.5	105.4	+4.1	0.0154	0.02479	495.8	105.4	+20.2
9			40		12	0.0198	0.03187	637.5	235.2	+35.3	0.0211	0.03397	679.4	235.2	+74.0
10		4	40		12	0.0189	0.03042	608.5	235.2	+6.3	0.0204	0.03284	656.8	235.2	+51.4
11		4	40	1000	12	0.0194	0.03123	624.6	235.2	+22.4	0.0208	0.03348	669.7	235.2	+64.3

fairly well through filter paper, but some of the sterilized soils in this experiment were too slow in filtering, hence the Chamberland Pasteur filters were used.

The soil residue in the shaker bottles was again treated with 500 cc. of normal NH_4Cl and shaken for three hours. The contents of the bottles were then filtered through the Chamberland Pasteur filters. The filtrates of the two extracts were mixed for quadruplicate analyses of 100 cc. aliquots. The aliquots were heated, made slightly alkaline with ammonium hydroxide, and precipitated with $(NH_4)_2CO_3$. After standing for a few minutes at approximately boiling heat, they were filtered through filter paper and the precipitates washed free from chlorides with hot, distilled water. From this point on the "official" J. Lawrence Smith method for potassium was followed.

The results of the averages of the quadruplicate analyses together with the treatments of the sterile and non-sterile soils, are reported in table 1. The amounts of soluble potassium added in the form of clover hay, manure or orthoclase are given in column 10 of the table. The relation of potassium recovered to the total amount found in the check plus the soluble forms in clover hay, manure, or orthoclase added in the various treatments, is given in column 11. The results are calculated in percentages and also in pounds per acre, one acre representing 2,000,000 pounds of surface soil. The manure used for the treatments contained 1.071 per cent of soluble potassium, the clover hay 0.981 per cent, and the orthoclase 0.0135 per cent.

With the exception of samples 4 and 5 in the non-sterile set, and 3 and 4 in the sterile set, all treatments yielded a decided increase in replaceable potassium. The decreases occurring with sample 4 of both the sterile and non-sterile set cannot be explained here, but the decrease for sample 3 of the sterile set may be due to experimental error.

The clover hay treatments, although applied in smaller quantities, gave better results than the manure treatments. Clover hay seems to be more effective than manure in liberating soil potassium.

The sterile set yielded more replaceable potassium than the non-sterile set. This brings up the question of the possibility of releasing replaceable potassium from the insoluble forms by means of sterilization. This point was cleared up by mixing two 500-gm. portions of air-dry Carrington loam, with 8 gm. of manure (16 tons per acre) and placing in bottles. Distilled water was added to bring the soils to the optimum. One sample was sterilized in the autoclave at 15 pounds pressure, for three hours in six intermittent sterilizations, the intermissions being 36 hours. The soils were then air dried and the replaceable potassium determined in the usual way. The results of quadruplicate determinations reported in table 2 give averages which are alike for sterile and nonsterile soils. Hence, sterilization had no effect on the replaceable soil potassium.

The larger amounts obtained in the sterile set may be due to the action of the decomposition products resulting from the application of heat and pressure on the organic matter.

The increased biological activities, so clearly indicated by the larger amounts of carbon dioxide produced in the previous investigation (4), but which showed no relation to water-soluble potassium, gave no indication of any relationship to the replaceable soil potassium. The largest increases in replaceable potassium were, with few exceptions, directly related to the largest applications of organic matter.

If the contentions of Kellner (3) and Hissink (1) are correct, namely that only water-soluble and absorbed potassium can be replaced and that both of these forms can be utilized directly by plants, then the increased amounts of replaceable potassium obtained in this experiment are directly due to the

TABLE 2

Replaceable potassium recovered from soil treated with KCl, and from sterilized and unsterilized soils

TREATMENT	WEIGHT OF K_2PtCl_6	AVERAGE K_2PtCl_6	K IN 50 GM. SOIL	K ADDED	K RECOVERED
	gm.	*gm.*	*mgm.*	*mgm.*	*per cent*
No treatment	0.0167 0.0188 0.0169 0.0195	0.0179	14.40	0	0
50 gm. KCl	0.0479 0.0466 0.0462 0.0468	0.0469	37.73	26.2	88.9
Not sterilized	0.0202 0.0201 0.0215 0.0200	0.0204			
Sterilized	0.0211 0.0200 0.0202 0.0204	0.0204			

effect of clover hay and manure. Furthermore, this method could be used as a reliable means of measuring the available soil potassium.

The increases indicated in table 1 are not very large, but it should not be overlooked that these results represent probably only about 90 per cent of the total replaceable potassium. This fact was ascertained by weighing four 50-gm. portions of Carrington loam in tumblers. Distilled water was added to bring the soils to optimum moisture conditions. Two of the soils received no other treatment, while the remaining two received 50 mgm. of KCl dissolved in the distilled water applied for optimum moisture purposes. The four samples were allowed to stand for 48 hours. They were then extracted according to the regular method used in this experiment.

The results of duplicate determinations reported in table 2 show that 88.9 per cent of the potassium applied was recovered in the two extracts. This fact may be used as a fair basis for estimating the results of the clover hay and manure treated soils. The gains shown in table 1 would increase considerably if calculated on a 100 per cent basis, and would surely be of practical value in farm practice.

CONCLUSIONS

The determination of replaceable potassium in sterile and non-sterile Carrington loam treated with varying applications of clover hay and manure lead to the following conclusions:

1. About 90 per cent of the absorbed potassium of Carrington loam was replaced by two extractions with normal NH_4Cl.

2. The application of organic matter, such as clover hay and manure, resulted in the liberation of considerable quantities of replaceable potassium from the soil. This liberation was increased proportionally to the increased amounts of organic matter applied.

3. The clover hay seemed to effect the liberation of replaceable potassium in a greater degree than the manure. This was observed in both the sterile and non-sterile soils.

4. The carbon dioxide production and the biological activities showed no relation to the liberation of replaceable potassium.

5. Sterilization had no effect on the replaceable potassium, but the sterilized soils, due probably to the effect of the decomposition products resulting from the application of heat and pressure to the moist organic matter, liberated more soluble potassium than the un-sterilized soils.

6. The liberation of replaceable potassium appeared to be largely a chemical process which seemed to proceed in the absence of biological factors.

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